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② FEASIBILITY STUDY REGARDING
LANDFILL OF NITROCELLULOSE LIME SLUDGE AND
OXIDATION OF NITROGLYCERIN WASTEWATER STREAM.

TECHNICAL REPORT CONTRACT NO.

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ABSTRACT

A study was begun to determine the fate of limed nitrocellulose (NC) sludge in a landfill situation and to establish the best method for oxidation of sulfides in a nitroglycerin wastewater stream. Prior to the initiation of a lysimeter study on the nitrocellulose sludge, a literature review was conducted to identify potential degradation products and establish a sensitive technique for analyses of nitrocellulose. It was determined that the chemical degradation of nitrocellulose in an alkaline environment was not a simple saponification reaction, but rather involved degradation to a variety of products. The analytical technique developed involved determination of nitrocellulose and other organic nitrate esters. The procedure included separation of the nitrocellulose, quantitative denitration of the organic ester and then analysis of the resulting nitrate using an automated cadmium reduction method. The procedure was tested and found to be repeated to $0.36 \text{ mg/l} \pm 0.01 \text{ mg/l}$ with average recoveries of 90%.

Twelve lysimeter columns were constructed and filled with underlying soil, sludge or a 50:50 sludge soil mixture and topsoil in various combinations. Dosing with rainwater was done at three different rates to simulate varying infiltration conditions. No nitrocellulose fines were leached directly, however, inorganic nitrate/nitrite concentrations up to 13,000 mg/l were found in the leachate. They were a result of both elutriation and continued degradation of the NC. The volume of leachate was extremely small, 0.021-0.068 bed volumes per month. Cyanide was found in the leachate in concentrations up to 20 mg/l. In all instances the sludge/soil produced a less contaminated leachate. The sludge contaminants changed over time. The NC continued to degrade chemically with the formation of complexed cyanide compounds. The sludge/soil systems showed evidences of microbiological denitrification with significant reductions in both nitrate and cyanide values. The subsoil acted as a filter which removed insolubles at the substrate/soil interface and allowed passage of only soluble constituents. Landfill disposal using a containment approach to minimize leachate production is recommended. A liner and leachate collection system may be necessary to comply with applicable regulations. The NC limed sludge should be mixed with soil to reduce permeability and enhance microbiological degradation.

The nitroglycerin wastewater stream was analyzed to determine the best method of lowering sulfide concentrations from approximately 100 mg/l to 10 mg/l. Laboratory tests indicated that chlorination with 700 mg/l free chlorine would effectively lower sulfide concentrations in thirty minutes. Scale up to handle the $178 \text{ m}^3/\text{day}$ (47100 gpd) flow rate indicated that direct injection of sodium hypochlorite into a separate 7.5 m^3 (2000 gal.) reaction vessel would be the most feasible approach if sufficient volumes of water for dilution were unavailable. Capital costs for this system are estimated to be \$16,560 with operating costs of \$31,360 annually.

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SECTION I

CONCLUSIONS

1. The literature reviewed indicated that the chemical degradation of nitrocellulose fines is not a simple saponification reaction but rather involves degradation of the nitrocellulose into many possible degradation products including: inorganic nitrates and nitrites, cyanide, nitrous oxide, carbon dioxide, ammonia, and various organic acids.
2. The other potential decomposition mechanisms as indicated in the literature review include potential biological degradation after modification with alkaline compounds. Anticipated by-products would include the mobile nitrate/nitrite ion which may adversely affect leachate quality.
3. A quantitative method for analyses of organic nitrate esters at concentrations of 1 mg/l was developed. The technique includes separation of the insoluble compounds by filtration, quantitative denitration with DMSO and analyses of the resultant inorganic nitrate using the automated cadmium reduction method.
4. Extremely high concentrations of inorganic nitrate/nitrite (ranging from approximately 8,000 - 13,000 mg/l NO_2/NO_3) are present in the leachate from the sludge and sludge/soil mixture. These are a result of both elutriation of existing nitrate and continuing chemical degradation of the nitrocellulose.
5. No nitrocellulose fines were present in the collected leachate and do not appear to migrate through or concentrate in the sludge systems.
6. The low permeability of the sludge and sludge/soil will attenuate the effects of the contaminant concentrations over an extremely long period of time.
7. The high concentrations of inorganic nitrate/nitrite adversely affect several common analytical methods including TKN, TOC and ammonia.
8. Cyanide is a substantial degradation product from the nitrocellulose. Most of the cyanide is present as complex organic cyanides and remains entrained in the sludge and sludge/soil. However, some free cyanide is leached through the substrate and was measured in the leachate in concentrations ranging from 1-20 mg/l.

9. Biological denitrification appears to occur in the sludge/soil system and reduces concentrations of TOC, nitrate/nitrite and cyanide in both the substrate and the leachate.
10. A disposal method involving minimal leachate production and isolation appears to be the best technique for landfill of a nitrocellulose sludge/soil mixture. This is referred to as the "containment approach". Though a leachate collection system may not be required because of hydrogeological features at the site, it may be required by regulatory agencies under landfill criteria for hazardous wastes currently being developed.
11. Oxidation of the nitroglycerin waste stream to reduce sulfide concentrations from 100 mg/l to less than 10 mg/l is most effectively accomplished using chlorination. Chlorine dosages of 700 mg/l were found to be effective in reducing the sulfide levels to less than 5 mg/l in thirty minutes.
12. Other oxidation techniques including aeration and oxygenation plus possible catalysis with UV light did not reduce the sulfide to desirable levels within a reasonable reaction time.
13. Dilution with an appropriate volume of a low sulfide containing wastewater stream is the most economical approach to sulfide reduction.
14. If dilution is not possible, then sodium hypochlorite can be added to the NG-1 wastewater stream in a separate tank. Feedback control based on the volume of wastewater to be treated is desirable. The total capital cost for the recommended chlorination system is \$16,560 with annual operating costs of \$31,360.

SECTION II

RECOMMENDATIONS

1. Sludge/soil mixtures should be evaluated to establish the optimum mixture to reduce permeability and enhance microbiological denitrification in the substrate. Some laboratory studies involving primarily denitrifier enumerations should be conducted to verify potential landfill approaches in this regard.
2. Tests should be performed to confirm the presence of denitrifying bacteria in the sludge/soil systems. If the results are positive, literature review of information related to soil microbiology should be made to determine what conditions are most conducive to the development of a high population of denitrifiers in the environment, and to determine if these conditions can be applied to potential NC lime sludge disposal areas.
3. An evaluation of anticipated volumes of NC lime sludge generated during normal and mobilization operations should be performed prior to design of a disposal facility.
4. The impact of new Federal regulations on the disposal options should be established as soon as final regulations are promulgated. Various disposal options should be reviewed and reevaluated for both technical and economic feasibility considering the effect of this legislation.
5. Landfill of nitrocellulose lime sludge should be performed in a manner to minimize leachate production. A lined area equipped with a leachate collection system will probably be necessary to comply with regulations.
6. Nitrocellulose limed sludge should be landfilled as a mixture of sludge and soil to enhance denitrification in the substrate.
7. A method for analyses of TKN in the presence of extremely high inorganic nitrate/nitrite concentrations should be developed.
8. If possible, the nitroglycerin waste stream should be diluted with large volumes of other wastewaters which also require biological treatment. The volume of dilution water needed is dependent on the sulfide concentration of the diluting wastewater and can be calculated using an empirical formula related to concentrations of sulfide in the nitroglycerin waste stream and the diluting stream.

9. If dilution is not possible, the recommended system for dilution should include direct addition of metered sodium hypochlorite to a separate 7.5 m³ (2000 gal.) reaction tank.

SECTION III

INTRODUCTION

The best method for disposal of nitrocellulose lime sludge generated during the manufacture of nitrocellulose propellant is not well defined. Various alternatives include open burning, controlled incineration, reduction with sodium hydroxide, and recovery by recalcination. These have been considered and none have been shown to be feasible in all situations. Therefore, landfill of the nitrocellulose (NC) limed sludge was considered a viable option. However, sufficient information was not available to evaluate this alternative. Specifically, the quality of the sludge, and the associated leachate needed to be determined. This project was performed to provide the needed information.

The feasibility of landfilling NC lime sludge was evaluated through a controlled lysimeter study. Prior to initiating the column study, a literature review was performed to aid in identification of possible decomposition products from the nitrocellulose in the highly alkaline lime environment. Methods for analyses of NC were also reviewed and found to be insensitive at the levels which must be measured. A new technique was developed for analyses of organic nitrate esters at low concentrations. Once the preliminary information was obtained, the study plan was finalized. Lysimeter columns were then constructed and filled with sludge and soil samples obtained from Radford Army Ammunition Plant. Rainwater was used for dosing the columns to reach field capacity and then to simulate rainfall conditions. The dosing period extended 22 months in order to obtain the necessary information. Results from the chemical evaluation of both the leachate and sludge substrates are presented in this report. The applicability of this information to potential landfill disposal options is also included.

In addition to studying the fate of the landfilled nitrocellulose lime sludge, a study was made of the NG-1 wastewater which contained high concentrations of sulfides. Since this waste stream was to be placed into a biological treatment system, sulfide concentrations greater than 10 mg/l were undesirable. The initial waste was anticipated to have concentrations of 100 mg/l sulfide which would inhibit growth of desirable microorganisms needed for biological treatment. Therefore, various methods for sulfide oxidation were tested and then evaluated with respect to their technical and economic feasibility. The results of this study have been completed and are contained in this report.

The remainder of this report has been divided into several sections to present the results in a logical fashion. Extensive data tables are

available as a separate Appendix.

SECTION IV - BACKGROUND INFORMATION AND OBJECTIVES OF THE STUDY

This section presents information on the generation of the NC lime sludge and the nitroglycerin wastewaters considered in this evaluation. The objectives of the project effort are also included.

SECTION V - LITERATURE REVIEW AND DEVELOPMENT OF ANALYTICAL METHOD FOR NITROCELLULOSE DETERMINATION

The results of a brief review of the literature regarding landfill systems, leachates, plus potential degradation products of NC are presented. The method development for establishing an analytical technique for measuring trace quantities of nitrocellulose and other organic esters is then discussed.

SECTION VI - COLUMN STUDY

The details of the column study are presented in this section. The column construction information is presented first followed by an in-depth discussion of the results. The application of the data to landfill disposal options completes the section.

SECTION VII - SULFIDE REMOVAL STUDIES

The final results from the sulfide removal study on the nitroglycerin stream are presented. The results from laboratory testing of the various oxidation techniques including economic and technical comparison are discussed. The section also includes final recommendation regarding the most feasible approach to sulfide removal.

SECTION IV

BACKGROUND INFORMATION AND OBJECTIVES OF THE STUDY

GENERAL

This report deals with two different areas of waste disposal at the Radford Army Ammunition Plant (RAAP) in Virginia. One portion involved the determination of the fate of nitrocellulose (NC) fines when limed NC sludge was placed in a landfill situation. Lysimeter columns were constructed and filled with Radford soil and sludge for this investigation. The second aspect of the study involved determination of the most feasible technique for reducing the sulfide content of the nitroglycerin wastewater stream. Both studies were conducted on samples of sludge or wastewater shipped from RAAP. In this manner, the most accurate determination of the actual response of the wastes could be established.

GENERATION OF NITROCELLULOSE LIME SLUDGE

Nitrocellulose is manufactured in a series of steps. A schematic of the operation of the batch system at RAAP is shown in Figure 1. The first step in the manufacture involves nitrating cotton linters in a mixed acid media (1, 2). From there, the material is boiled in acid and neutral baths and then washed with recovered filtered water. This water is discharged to boiling pits and sent to an acid recovery system. The NC is then slurried, neutralized with a small amount of sodium carbonate and pumped through primary and secondary Jordan beaters. From the beaters, the slurry is pumped into the poachers where the NC is boiled in a soda ash solution at elevated temperatures for several hours followed by a clear water boil. The treated NC is settled for an hour and separated, then the liquid and NC fines are sent to poacher tanks.

From the poachers, the NC is vacuum filtered and reslurried in the blender house for 5 hours. The final NC product is sent to the wringer where the moisture content is reduced to approximately 70% liquid (30% solids). A portion of the product is sent to alcohol rectification where a higher quality material is obtained using water displacement by alcohol in dehydration presses. The liquid from this process also contains fines which must be disposed of or recovered.

Both batch and continuous nitrocellulose production operations are presently in use at RAAP. The continuous process involves continuous nitration followed by centrifugation, although the other steps are the same as the batch system. Because the nitrocellulose manufacturing process uses large volumes of water, 132-8321/kg (16-100 gal./lbNC)(2), a significant effort has been

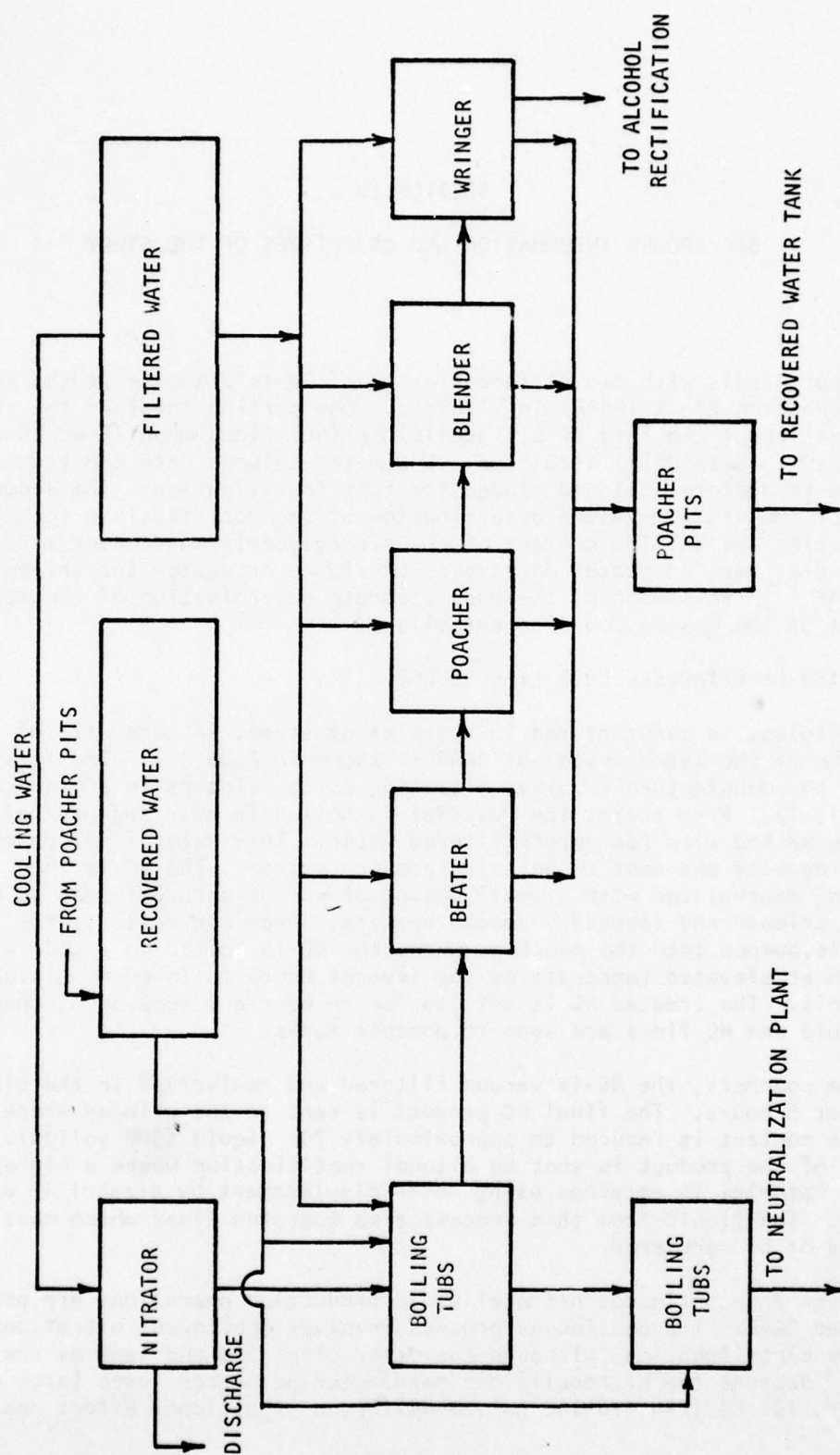


Figure 1. Water streams in batch nitrocellulose operations (2).

made to reduce the amount by various recycle and re-use techniques. Centrifuge separators have been installed at the poacher tanks to separate the fines from the water prior to re-use of both streams. The continuous NC line also uses less water.

Use of centrifuges at the poacher pits has eliminated this area as a source of fines, however, there are still fines generated from the alcohol rectification area. Treatment of these materials has involved addition of lime and other chemicals to neutralize acidic streams and entrain and precipitate the NC fines. The NC sludge utilized for this study was generated by lime treatment of alcohol rectification wastewater. The sludge was then dewatered by vacuum filtration with a resultant cake solids concentration of approximately 35-40%.

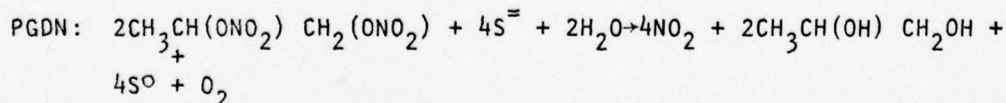
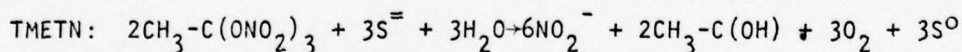
GENERATION OF NG-1 LIQUOR FOR SULFIDE STUDIES

The nitroglycerin waste stream consists of wash waters and mixed acid nitrating solutions which are needed for the purification process in nitroglycerin manufacture. Prior to discharge of this waste stream, the entrained nitroglycerin must be decomposed or denitrated. The mixed stream (NG-1) at Radford contains the following nitrated esters (3).

- a. Propylene Glycol Dinitrate (PGDN)
- b. Triethylene Glycol Dinitrate (TEGDN)
- c. Trimethyl Ethane Trinitrate (TMETN)
- d. Trimethyl Ethane Dinitrate (TMEDN)
- e. Trimethyl Ethane Mononitrate (TMEMN)

The individual concentration of these esters varies in both volume and concentration. Prior to release, all of the nitrated esters must be desensitized and the metals concentration must be reduced.

Several methods are available to desensitize the nitrate esters including hydrolysis with lime, ozone oxidation and reduction with sodium sulfide. The preferred method at Radford for the NG-1 stream involves addition of both lime for metals precipitation and sulfide to denitrate the esters. The sulfide reaction mechanism is theoretically written as follows (3):



The theoretical sodium sulfide demand is 0.55 kg (0.55 lbs) per kg (pound) TMETN and 0.66 kg (0.66 pounds) per kg (pound) of PGDN. Laboratory studies indicated that the demand was 1 kg (1 pound) per kilogram (pound) of nitrated ester and that the reaction was catalyzed by hydroxyl ions in solution (3).

It was anticipated that this waste stream, after denitration would be directed into a biodisc biotreatment system. Since sulfide is toxic to microorganisms at concentrations greater than 10-25 mg/l, it was necessary to lower the sulfide concentration levels from the 100 mg/l residual concentration anticipated. Several methods were available and they are discussed in detail in Section VII along with the results of the study which indicated the most feasible oxidation technique.

OBJECTIVES OF THE STUDY

There were three main objectives of this study:

1. Determination of the fate of nitrocellulose fines from a limed sludge when placed in a landfill situation.
2. Establishment of the potential leachate quality associated with two mixtures of landfilled nitrocellulose limed sludge.
3. Recommendation of the most economically feasible method for oxidation of sulfide in the NG-1 waste stream to lower sulfide concentrations to less than 10 mg/l.

These objectives have been met during the course of this study and the results are presented in the remainder of this report. The various full-scale disposal options for nitrocellulose sludge are also discussed in view of current regulatory requirements.

SECTION V

LITERATURE REVIEW AND DEVELOPMENT OF ANALYTICAL METHOD FOR NITROCELLULOSE DETERMINATION

INTRODUCTION

The purpose of this portion of the project was to determine what information was available regarding the degradation characteristics of nitrocellulose-lime sludge in a sanitary landfill. Concomitantly, an ancillary literature survey was made to determine the feasibility of developing and testing an analytical method for determining nitrocellulose (NC) and its organic nitrate ester decomposition products in the landfill leachate.

Because there was no specific work on nitrocellulose-lime degradation in the soil regime reported in the literature, it was possible to only infer likely degradation paths based on a knowledge of how NC-lime sludge is generated. The fact that the manufacturing process utilizes an acid environment and the waste treatment system employs lime indicates that the mechanisms of acid and alkaline decomposition could influence the chemical degradation of NC. The degradation studies cited were generally conducted under more severe conditions than could be expected to evolve in a subsoil matrix although the time frame for degradation in the soil would be much longer. Given these constraints it is reasonable to assume some of the cited degradation products may occur in the leachate or, as in the case of the inorganic nitrate ion, enrich the subsoil environment and promote the growth of denitrifying bacteria.

A method for determining NC and related organic nitrate esters at trace levels (1 mg/l) using the nitrate ion as a tracer is proposed. The method involves separating the inorganic nitrate ions from the organic nitrate by filtration, quantitative denitrification of the organic nitrates and measurement of the resultant inorganic nitrate by a conventional wet chemical technique. After the tentative technique for NC analysis was developed, it was carefully tested prior to application in the leachate analysis.

SANITARY LANDFILL AND LEACHATE

A sanitary landfill can be described as a disposal operation where solid wastes are placed in an excavated site and covered, ideally, without causing pollution or nuisance problems. Most of the research on sanitary landfills has been done on a municipal refuse. Only in recent years has there been an interest in landfilling of materials generally classified as hazardous, such as nitrocellulose. The most potentially polluting aspect of a sanitary landfill is liquid discharge (leachate) which can

occur from precipitation which percolates through the disposal site, carrying dissolved and suspended organic and inorganic material into groundwater supplies. The amount of leachate generated depends on the size of the landfill, the nature of the refuse, and the permeability of both the cover soil and the subsoil regime. The quality of the leachate is also a function of the refuse type, as well as the rate of leachate flow through the system. The leachate passing through the refuse mass absorbs organic and ammonia nitrogen and phosphorus from the organic matter. It also solubilizes many inorganics which are present including calcium, magnesium, sodium, potassium, iron, chlorides, sulfates, etc. Some of these go into solution slowly, while others are very soluble. The elements and ions listed are the most common, however, considering the possible variations in the solid wastes and employing analysis procedures to trace levels, a vast array of substances can be found in landfill leachates.

Leachate Production Mechanism

A number of conditions must be satisfied before a leachate and gases are produced in a solid waste land disposal site. In addition to refuse mass already discussed, adequate moisture, microorganisms, and suitable conditions for microbial activity are necessary. Municipal solid waste generally contains 20 to 30 percent moisture by weight. This moisture is sufficient to cause active decomposition but not necessarily the most optimum rate. Approximately 50 to 60 percent moisture is required for this situation, which is the reason this value is used for composting operations. The level of moisture found in municipal refuse is generally not sufficient to generate a "flowing" leachate. Moisture from another source is necessary to accomplish this. In other words, the field capacity of the refuse must be reached before a leachate is produced.

The added moisture needed to satisfy the field capacity* of the refuse can originate from two sources: (1) the infiltration through the soil cover of water from precipitation or snowmelt, and (2) the upward or lateral movement of groundwater through the refuse mass. Both sources of this moisture are subject to control since they are to a large extent related to original site selection and subsequent engineering of the site.

The field capacity of refuse depends mainly upon its density and composition. Fungaroli (4) presented a summary of some published values and they vary markedly. For purposes of discussion, a municipal refuse with a dry density of 139 kg/m^3 (400 lb/yd^3) can have a field capacity ranging from 25-58 cm/m (3-7 in./ft) which is equivalent to a moisture content of 50% to 75%. As noted, this moisture range is close to the one cited for optimum microbial activity. Thus the level of moisture needed to produce

* Field capacity is defined as the moisture content of soil after gravity drainage is completed. The non-homogeneous nature of refuse frequently results in channeling of water, and thus leachate production before the entire refuse mass reaches field capacity. This is less likely to occur with milled refuse.

leachate flow through the refuse mass is close to the level at which the optimum production of leachate constituents also occur. Interestingly, Hughes et al. (5) following their examination of four landfill sites in northeastern Illinois, estimate that sufficient rainwater probably infiltrates through the soil cover to bring 1.2-1.5m (4-5 ft) of refuse to field capacity each year.

The microorganisms normally present in the refuse and those indigenous to the soil are sufficient to start the degradation of the organic fraction of the refuse. The decomposition process is usually aerobic for an initial period immediately following refuse decomposition. The activity is aerobic because sufficient molecular oxygen is present in the refuse mass due to low moisture and limited compaction. During aerobic decomposition the principal end products are carbon dioxide, water and a large array of oxidized inorganics such as nitrates, sulfates, and phosphates. If a leachate is generated during this phase of decomposition, it will contain many of these same oxidized end products. Microbial activity also results in a significant increase in temperature of the refuse mass. Depending upon the moisture content, temperatures in the range of 43.3-54.4°C (110-130°F) are not uncommon. These temperatures are sufficiently high to cause the destruction of many enteric pathogens if they happen to be present in the deposited material.

After a period which would vary anywhere from weeks to several months, the microbial activity changes to the anaerobic type. This change is brought about by an increase in moisture and degree of compaction, which in turn results in the depletion of molecular oxygen from the refuse interstices and restricts the passage of a renewed supply from the atmosphere. At almost all landfill sites there is little question that virtually all of the degradation activity is of the anaerobic type. The principal end products of this activity with the exception of carbon dioxide and water are of the reduced form. They include among others methane, ammonia, nitrogen, sulfides, organic and amino acids, plus a large array of other such materials. Except for non-soluble gases like methane and nitrogen, these are the types of materials which will form the constituents of leachate. This activity also results in an increase in temperature though usually not to the same magnitude as the aerobic phase. These temperatures are nonetheless sufficiently high to cause the destruction of some enteric pathogens.

Leachate Attenuation in the Soil Regime

There is no question that if the raw leachate is generated in a site where it can be channelized directly to a nearby ground water body, the water in the immediate vicinity of this area will be altered markedly in quality. If there is a ground water user in this area, the water could be impaired for domestic or other uses. This situation reflects a poor landfill design from three standpoints; (1) poor site geological features, (2) limited distance between the point of leachate generation and ground water body, and (3) close proximity to a ground water user. In a properly selected and operated site these events should not occur because of a natural "attenua-

tion mechanism" afforded by the soil regime.

The attenuation mechanism is a rather complex interaction of physical, chemical and biological forces, some of which have been identified and studied, other of which are poorly understood and in need of in-depth study.

What is known is that the overall effect of the soil regime results in an attenuation of the grossly polluted leachate to a level where the impact on the ground water is reduced to a tolerable or acceptable level. The mechanism can be described as follows: The soil provides the site for active microbial degradation of the organics that are present in the leachates. Some inorganics are adsorbed to the soil surface, and many of the more undesirable ions are exchanged for the more desirable ones. Both the adsorptive and exchange properties of soils can vary greatly from site to site. Clay type soils exhibit these properties to the greatest extent. Heavy metals, and to a certain extent calcium and magnesium, tend to be held to soils, whereas cations like sodium and potassium are more likely to be released. The extremely low velocity of the underground water resource provides the necessary time for these activities...especially the microbiological ones...to reach a fair degree of stabilization, thus confining most of the degradation processes to the immediate vicinity of the landfill. The soluble end products can be attenuated even further by the sheer vastness of the underground water body through the simple mechanism of dilution. The highly soluble chloride ion provides a useful tracer for the situation described above.

Unfortunately, the attenuating mechanism described above does not hold true to the same degree for all geological formations, and therein lies the crux of the problem. The above will usually hold true for unconsolidated formations consisting of varying proportions of clay, silt, fine sand, and loam with low to medium permeabilities. For unconsolidated materials of coarse sand and gravels with high permeabilities or consolidated materials such as limestone or shale with fissures, faults, or fractures of any kind, the protective mechanism breaks down because of time. In unconsolidated formations, there is much less time available for the degradation process to take place within the vicinity of leachate generation areas because the underground velocities are much higher. It is in these areas, of course, that the potential for groundwater pollution is the greatest.

A properly designed landfill site is one in which the velocity of leachate travel is sufficiently low to insure that the attenuation mechanism is operative. In other words, the soil regime should have a suitable "permeability". The unit of permeability, cm per sec., is nothing more than a velocity unit. The U.S. Environmental Protection Agency (6) suggested suitable permeabilities for landfill sites. Hughes (7) for example, has suggested that permeability values of approximately 10^{-6} cm per sec. will "retard" movements of leachate constituents. This means that soils consisting of silts, mixtures of sand and silt, and clays are usually suitable. It is important to note that as the permeability of soil decreases, the average grain size is also decreasing. In general, soil adsorption and ion exchange potential increase with a de-

crease in soil grain size. Thus the biological, physical and chemical forces operative in the attenuation mechanism are all enhanced (up to a point short of total flow restriction) with decreasing permeability of grain size.

NITROCELLULOSE - LIME SLUDGE BACKGROUND

Nitrocellulose Manufacturing and Physical Properties

Cellulose polymers of varying chain length and cross linkages in the form of wood cellulose or cotton linters are treated with a mixture of sulfuric acid (59-67%), nitric acid (21-23%) and water (10-20%) to form the nitrate ester of cellulose designated NC. The degree of nitration is determined by batch contact time, mixed acid ratios and the cellulosic backbone with a minimum theoretical yield of 14.15% N by weight. In practice NC polymers containing between 12.6% N and 13.4% N are designated as "gun cotton" or "smokeless powder" and are used as propellants in the pyrotechnic industry. Due to its cellulosic backbone, NC is not a simple chemical compound but rather it is a class of nitrated cellulosic polymers defined by the physical-chemical properties indicated below.

Molecular Weight: variable, about $273.3n$ where n = degree of polymerization

Chemical Formula: $(C_6H_{10-x}O_5-x(ONO_2)_x)_n$ for 12.6%N $x = 2.45$

Color: white

Density: about 1.66 g/l

Solubility: acetone, ether-alcohol (2:1), nitro compounds, organic nitrates, fatty acid esters, insoluble in water

Flash Point: (closed cup) 40°F

Heat of Combustion: 2409 Kcal/kg

Once nitrated, the NC must be washed with copious amounts of water to remove the excess reaction by-products, adhering nitric and sulfuric acids and NC fines. The Radford arsenal has evaluated a pilot system for treating such a waste wash water with lime and other chemicals, followed by vacuum filtration. The sludge (NC-lime sludge) generated by the process has been designated for possible disposal by landfill. The purpose of this phase of the study is to examine and report on literature which deals with the degradation behavior of NC in the NC-lime sludge landfill so that the potential impact of leachate from the landfill can be better evaluated.

NC Degradation

Due to NC's insolubility in water, its mobility and ultimate fate in soil matrix will be predicted on its susceptibility to chemical and/or biological degradation.

Chemical Degradation - The NC-lime sludge generated from the process described in the previous section may contain NC fines, lower nitrated cellulose, various organic compounds endemic to the nitration process which originates from the cellulosic decomposition in the mixed acid media,

and nitrate and sulfate ions from the residual mixed acids (8, 9, 10, 11).

Mudrack's (8) study of industrial NC wastes treated with lime indicated that a large portion of the sulfate ions were removed from the waste stream in the form of the relatively insoluble CaSO_4 moiety. The nitrate ions remained dissolved in the waste suggesting that the NC lime sludge would contain higher concentrations of sulfate ions than nitrate ions, since nitrate would be removed in the effluent. The liquid entrained with the sludge could, however, contain large quantities of nitrate.

The NC fines, as well as lower nitrated organic by-products in the NC lime-sludge, may be subject to chemical degradation by alkaline decomposition due to nature of the lime sludge cake. Kenyon and Grays' (11) early study of NC alkaline decomposition reported that the reaction was not a simple saponification which typically occurs with esters in an alkaline environment but rather yields a series of oxidation products and low molecular weight, lower nitrated cellulosic chains. Their studies reported that 10g of NC required 245 hours to completely decompose at 30°C in a 1% NaOH solution. During this period, relatively small amounts of CO_2 were liberated and 60% to 70% of the nitrate groups were reduced to the inorganic nitrate form. Urbanski (9) in summarizing the work of authors who had studied the alkaline and acid hydrolysis of NC, enumerated the following compounds as possible degradation products: inorganic nitrates and nitrites, cyanide, nitrous oxide, nitrogen oxides, carbon dioxides, carbon monoxide, ammonia, and the organic acids; oxalic, malic, formic, glycolic, butyric, malonic, tartaric, trihydroxyglutaric, dihydroxy-butyric, hydroxypyruvic, saccharic and tartronic. The NC polymer chain has reportedly undergone hydrolysis by water at ambient temperatures (9). The highly acid manufacturing process and subsequent entrapment in the weakly alkaline lime sludge would expose NC fines to both acid and alkaline degradation. The mobility of these degradation products would be a function of their solubility in the leaching water or their ability to adhere to or form organo-clay complexes and be mechanically carried through the soil environment into the ground water supply. Undergraded NC fines which are leached from the NC-lime sludge into and retained by the relatively mild chemical environment of the sanitary landfills underlying soil matrix would not be expected to undergo as much chemical degradation. Such degradation would more likely occur either during the manufacturing steps or in the lime sludge generated by the waste treatment process.

Photochemical decomposition occurs by means of chain lysis as well as denitrification and can be induced by sunlight or UV light. Urbanski (9) reported that the decomposition rate of 13.3% NC when exposed to UV light fits an exponential equation. Photochemical decomposition would most likely not play a significant part in sanitary landfill studies because of the limited exposure the NC-lime sludge would have to direct sunlight before being covered by backfilled soil.

Biological Degradation - Early work indicated that some molds (*Aspergillus*) could grow on moist NC (9). However, further investigations established that only the mineral salts adhered to the NC were being utilized by molds and microorganisms, not the NC itself. Extensive work on the biodegradation

of NC by Wendt (12) and co-workers at the Army's Natick laboratory indicated that the unmodified NC compound was resistant to biological degradation. However, after modification with NaOH, the chemical degradation products were amenable to microbiological utilization.

The inorganic nitrate ion will likely be the most mobile (by virtue of its high solubility) and therefore the most probable nutrient to be leached from NC lime sludge. Given a carbonaceous source, perhaps from other NC degradation compounds, and the anoxic conditions of a subsoil matrix, enrichment for denitrifying bacteria may occur. In the previously cited work of Mudrack, (8) the nitrate rich wastewater, after treatment with lime to remove the sulfate ion, was fed to a reaction tank where mechanical aeration was replaced by slow mix agitation. Oxygen necessary for the bacterial oxidation of the organic portion of the waste was supplied by the nitrate ion, resulting in the liberation of N_2 gas. Mulbarger (13) in his studies of denitrifying bacteria in waste treatment systems established the optimum pH range for these microorganisms to be 6.5 to 7.5. Within this pH range and at a temperature of 20°C, denitrifying occurred (at the rate of about 1 kg of oxidized nitrogen removed/day/kg of mixed liquid suspended solids). If the buffering capacity of the underlying soil is poor or a readily oxidizable source of carbon is not available, denitrification in the soil matrix would be expected to proceed exceedingly slowly, resulting in the release of nitrate/nitrite nutrients from the landfill.

ANCILLARY STUDY FOR NITROCELLULOSE ANALYSIS

The problem of developing a method which is specific and sensitive for nitrocellulose is that, as is inferred in the previous section of this survey, NC is not a specific chemical entity but rather a class of compounds which fall within a range defined by the degree of nitration as well as the polymer chain length of the cellulosic backbone.

Infrared spectroscopy has been successfully employed for the determination of cellulose nitrate in paint lacquers where the stretching valence vibration of the NO_2 group occurring at either 6.05 μm or 11.8 μm are measured (14)(15). Distortion of the 6.05 μm band by carbonyl groups at 5.8 μm , and broad interferences which are present in an environment matrix and occur at the 11.8 μm band, limit the application of these methods for this study. Ages and Bowen (16) were able to overcome these interferences by using N-N dimethyl acetate as a solvent and employing the method of standard addition, however, the resolution of added concentrations would make its application too insensitive for determining trace amounts of NC.

A review of assay methods typically employed in the quality control of nitrocellulose production i.e., gravimetric ignition techniques, nitrimeters, and others, lack the specificity or sensitivity necessary to determine potential trace amounts of NC in leachate (17). Total organic carbon analysis has the necessary sensitivity but it relies on the organic carbon as a tracer of NC in a system (soil leachates) where organic carbon abounds and therefore the method lacks specificity.

Sensitive and specific methods do exist for the determination of NO_3^- and NO_2^- in wastewater samples (18) and techniques are available for the denitri-fication of organic nitrate esters to inorganic NO_3^- (after the method of Smeenk (19)). A combination of these two techniques would provide a sensitive and specific method of determining not only NC but also some of its lower nitrated degradation products, reporting them as class of compounds (organic nitrates as N).

The problems anticipated in this study included, 1.) separating the inorganic NO_2^- and NO_3^- ions from the organic nitrates and 2.) verifying the recovery and precision and accuracy of the techniques by the use of spiked samples.

Separation of Organic Nitrate from Inorganic Nitrate

Initially, separation by liquid-liquid partitioning into a suitable immiscible solvent was considered, however, because of the slow disper-sion of NC into solvents and the differing solubility of the lower nitrated decomposition products, the probability of finding a broad range suitable solvent was low.

Separation of the insoluble organic esters by filtration was then evalu-ated. The widely used M-F Millipore filter of 0.45 μm pore diameter was not used because it is made from the cellulose acetate ester which in-terfered with the DMSO (Dimethylsulfoxide) reaction and contributed an unusually high nitrate blank. The filter media of choice was the glass fiber (Reeve Angel grade 934 AH) because of its inertness to chemical reaction and its low nitrate contribution when run as a blank. Glass fiber filter blanks averaged only 0.01 mg/l $\text{NO}_3\text{-N}$. The major disadvantage in using the glass fiber filters is the larger distribution of pore sizes compared to the cellulose acetate filters. This could have resulted in poor retention of the insoluble nitrate esters, however, as the recovery data presented later in the report indicates, the glass fiber filter quantitatively removed the nitrate esters.

Hydrolysis of the Organic Nitrates

Once the organic nitrate esters have been separated from the inorganic nitrate and nitrate ions, they can be quantitatively hydrolysed using DMSO in an alkaline media (19). The inorganic nitrate is prevented from being further reduced by adding hydrogen peroxide to the system (20). It was determined that aliquotes of 1 ml of DMSO, 1 ml of hydrogen peroxide and 0.2 ml of 7.5 N sodium hydroxide added to a 250 mm x 30 mm pyrex test tube were adequate for quantitative hydrolysis of the nitrate esters present on the glass fiber filter. The amount of hydrogen peroxide added to the glass fiber filter was reduced to 0.5 ml to prevent excess hydrogen peroxide not used in the blank reaction from interfering with nitrate/nitrite analysis on the Technicon Autoanalyzer II (AAII). A closed reaction vessel was not necessary for the sought after inorganic nitrate/nitrite ion. This system was used with success throughout the project. Although the possibility of a violent reaction was real and present, none occurred in the 22 months that the method was used.

Quantitation of the Hydrolysed Nitrate-Nitrite Ion

The modifications to the basic procedure to date have been with the intent of minimizing reagent blank values and interferences which could occur when quantitating the inorganic nitrate nitrite ions using the automated cadmium reduction method as given in the EPA Method for the Analysis of Water and Wastewater, 1976, p. 207 (18).

Throughout the procedure development period, collodion (USP grade) was used as the organic nitrate ester. The collodion, which was 11.1% N by weight was coated on Radford subsoil, ground in a mortar and pestle and sieved using a U.S. number 45 sieve. The referee analytical method involved firing aliquotes of coated and uncoated soil (after drying at 103°C) in a muffle furnace at 550°C. The difference in total volatile solids (TVS) was multiplied by the 11.1% nitrogen content of the collodion to yield the organic nitrate as N by dry weight of the soil. The soil of known collodion content was then dispersed in deionized water and an appropriate aliquote filtered and taken through the DMSO/AAll method. The results of the various modifications are presented in Table I.

The values given in Table I were the result of using 0.1N sulfuric acid to make the reactants up to 50 ml volume after the DMSO reaction. It was felt the acid media would act as a preservative for the inorganic nitrate. The data indicated a 96% recovery based on the referee method (TVS) however, the reagent blanks averaged 5% to 10% of full-scale on the AAll in spite of attempts to match the standard and sample matrices. The diluted reactants were then neutralized to a pH of 5-8 in an attempt to reduce reagent blank influence. The data in Table I shows that this method also gave quantitative recoveries when compared to the TVS method however, the variation (standard deviation) was higher and neutralization was time consuming. The reagent blanks were lower, in the range of 1% to 5% full-scale on the AAll. Part c of Table I is the most recent modification which involves direct dilution of the reactant before analyzing on the AAll. The standards and wash water were adjusted with 1.6 g/l NaOH to match the sample matrix. While the recoveries were somewhat less than those for the other two methods, the reagent blanks were typically less than 1% full-scale deflection. Each of the variations were evaluated in the presence of inorganic nitrate ions at approximately ten times the organic nitrate concentration to determine the specificity of the method for organic nitrates. There was no quantifiable interference.

As stated previously, the purpose of the hydrogen peroxide was to prevent the hydrolyzed inorganic nitrate ion from being further reduced. A series of inorganic nitrate solutions of known concentration were carried through the procedure to evaluate the effectiveness of the peroxide. Recoveries ranged from 85% to 110% indicating there was little or no reduction of the nitrate/nitrite ions.

A summary of the proposed method for the analysis of organic nitrate esters is given in "cook book" form as follows.

TABLE I. ANALYTICAL METHOD DEVELOPMENT, ORGANIC NITRATE AS N.

(Substrate: colodion coated, sieved Radford subsoil).			
a. <u>0.1 N H₂SO₄ as dilution water, (results as % N based on dry soil weight)</u>			
	<u>DMSO/AII</u>	<u>TVS</u>	
\bar{x}	0.26%	0.27%	
	0.02	0.03	
b. <u>Neutralization of dilution water (results as % N based on dry soil weight)</u>			
	<u>DMSO/AII</u>	<u>TVS</u>	
x	2.82%	2.86%	
s	0.42	0.27	
x	0.57%	0.51%	
s	0.16	0.04	
c. <u>Direct dilution (results as organic nitrates as N mg/l)</u>			
	<u>DMSO/AII</u>	<u>TVS</u>	
x	0.36 mg/l	0.40 mg/l	
s	0.01	0.04	

1. Principle.

Organic nitrate esters undergo rapid hydrolysis in the presence of dimethylsulfoxide (DMSO), water and alkali (19). Howard (20) has demonstrated the presence of hydrogen peroxide can prevent the inorganic nitrate from being further reduced to nitric oxide, nitrogen and ammonia. Smeenk (19) reported successfully using the technique in a modified Devarda analysis for determining the nitrogen content of various nitrate esters. This method employs the DMSO reaction on insoluble organic nitrate which might occur in an environmental matrix. The insoluble organic nitrates are removed from the aqueous media by filtration, hydrolysed and the resultant inorganic nitrate is quantitated using the automated cadmium reduction method.

2. Reagents.

- a. 30% H_2O_2 .
- b. DMSO (dimethylsulfoxide) - Aldrich Chemical.
- c. 7.5 N NaOH.

3. Apparatus.

- a. Reeve Angle glass fiber filter, 2.1 cm grade 934AH or equivalent.
- b. Porous Gooch crucible, filter type.
- c. 250 x 30 mm pyrex test tubes.

4. Instrumentation.

- a. Technicon AAll with nitrate/nitrite module (cadmium reduction method).

5. Procedure.

a. DMSO reaction.

1. Filter a representative sample aliquot (50 ml) through the glass fiber filter and wash with 200 ml of deionized water to remove any traces of inorganic nitrate or nitrite present in the sample.

Wash glass fiber filter for blank with the same amount of deionized water.

2. Place the filter in the 250 x 30 mm test tube and 1 ml of DMSO, 1 ml peroxide (use 0.5 ml peroxide on blank), and carefully add 0.2 ml 7.5N NaOH. The reaction will proceed within 2-5 minutes of the addition of the NaOH.
3. Dilute the reactants to 50 ml with deionized water and mix well. This should be done in a 50 ml graduated cylinder

and the final aliquot transferred back to the reaction test tube.

b. AAll

1. The Technicon should be set up per EPA Method for the Analysis of Water and Waste Water, 1976, page 207 with the exception that the wash water and standards should contain 1.6 g NaOH/l. The module should be set up for nitrate and nitrite quantitation.
2. Do not filter reacted samples to remove glass fibers.
3. A reagent blank should be subtracted from each set of analysis.

6. Calculations.

$$\frac{50 \text{ ml}}{\text{mls of sample filtered}} \times \frac{\text{NO}_3\text{-N in mg/l}}{\text{from the AAll}} = \text{Organic nitrate-N mg/l}$$

7. Precision and Accuracy.

Seven replicates averaged $0.36 \text{ mg/l} \pm 0.01 \text{ mg/l}$. Recoveries of known amounts of pyroxylin coated on soil averaged 90%. Three sets of seven replicates at concentrations of 1.6-2.6 mg/l had a standard deviation of ± 0.558 . Homogeneity of variance was evaluated before pooling according to the Cochran's test.

The method has been used to determine the residual cellulose nitrate concentration in the NC-lime sludge, as well as the column leachates in the presence of large inorganic nitrate concentrations. Analysis of composite samples have indicated that there are no organic nitrate esters, including nitrocellulose, apparent in the leachate. In order to confirm this observation, additional tests were performed on the method.

First, the ability of the method to quantitatively denitrify was tested using picric acid (2, 4, 6-trinitrophenol). Aliquots of picric acid were taken through the denitration procedure and analyzed. Recoveries of 80% of the theoretical organic nitrate was obtained, indicating that quantitative denitration had occurred.

Another test involved analysis of sample filtrate for inorganic nitrate before and after denitration. Aliquots of NC-lime leachate samples were passed through glass fiber filters. The filtrates were then split into two fractions. One fraction was analyzed for inorganic nitrate, the other fraction taken through the denitration procedure before analysis. No significant difference in the concentration of inorganic nitrate was found in the filtrate fractions. This indicates that any organic nitrates present were being retained on the glass fiber filters.

The method, shown to provide quantitative denitration, was then applied directly to the leachate samples. Tests were conducted involving the analysis of samples for inorganic nitrates both before and after the denitration reaction had occurred. Results indicated no significant increase in nitrates after denitration. This supported the analytical evidence that organic nitrate esters were not present in leachate samples in quantifiable amounts.

SECTION VI

COLUMN STUDY

GENERAL

The lysimeter study of the fate of nitrocellulose lime sludge was the major effort in this project. The columns were constructed, filled, dosed to reach field capacity, regularly dosed for 18 months and then dismantled. Discrete and composite samples of the leachate were collected over various time periods and then analyzed for different chemical constituents. No NC fines were found in the leachate, however, there were high concentrations of nitrate/nitrite and TOC measured. The results are presented in detail in this section of the report.

CONSTRUCTION OF THE COLUMNS

The columns were constructed from 15.2cm (6") I.D. PVC pipe in various heights. After fabrication, leak tests were performed and caulking was added. The individual tasks are described as follows.

Fabrication Steps

The materials needed for construction of the columns were ordered from local suppliers. Wall and base supports were specially fabricated and then shipped to the column site. The remaining materials were received and the columns were assembled. Twenty columns were assembled; 8 of which were 3.66 m (12 ft) long, 8 of which were 1.83 m (6 ft) long and four which were 2.29 m (7.5 ft) long. The different length columns were used to simulate different landfill conditions. The study columns were constructed of two pieces of 15.3 cm (6 in.) diameter PVC pipe joined by a PVC sleeve and appropriate gasket. The columns were supported on specially fabricated iron stands and secured by wall supports. To prevent or reduce short circuiting of rainwater through the column, 1.27 cm (1/2 in.) internal ribs made of RTV were cemented to the columns, 0.3 m (1 ft) from the end of each section. At the bottom of the column, a 15.2 cm (6 in.) base, tapered to a center hole, was secured. A fitting and plastic tube directed any leachate into a covered Erlenmeyer flask for collection. The columns were covered with caps to prevent excessive evaporation. A measured volume of rainwater was directly poured on the surface of the columns during the prescribed dosing periods. A port was provided in the column to allow removal of a sludge sample if necessary. Pictures of the components and columns in construction are shown in the Appendix.

Materials for Column Loading and Dosing

The underdrain systems for all columns was the same. Located at the bottom of the column was 20.3cm (8 in) of washed gravel graded from 2.54cm (1 in) at the bottom to 0.64cm (1/4 in) at the top. This gravel was covered with 10.2cm (4 in) of washed torpedo sand. Above this layer, in the appropriate columns, was 1.37m (4.5 ft) of underlying soil sample from the Radford landfill site. Then a layer of sludge or sludge/soil was placed in the 3.66m (12 ft) columns. All columns were finished with 0.46m (1.5 ft) of Radford top soil.

Rainwater collected from suburban area homes was used to dose the columns. This actual rainwater more closely simulated actual landfill conditions. It was stored in the laboratory refrigerator for periodic use.

Leak Test

After the columns were constructed, they were tested for possible leakage by filling them with water. Some leaks were discovered and corrected with additional caulking. There was an apparent problem, however, associated with the rubber stopper used to close the sludge sampling port in the column. This stopper was difficult to seal, however, once the columns were filled, the seal was improved.

LOADING OF THE COLUMNS

Initial Investigation To Obtain Soil

Soil used in the study was obtained from Radford Arsenal so the lysimeter study would more closely simulate the field conditions. Project personnel visited the arsenal to identify proper locations for soil sample collection.

Radford Arsenal presently has three separate disposal site locations. The first site is a non-combustible site for handling dirt, rocks, etc. which are removed during the various construction operations. The second site is the fly-ash landfill. This site may be utilized for ultimate disposal of the NC limed sludge. The topsoil layer is approximately 0.61m (2 ft) deep with a 0.61-1.83m (2-6 ft) clay layer beneath. This is underlain by a sandy layer 3.05-4.58m (10-15 ft) in depth. The lowest visible layer was a shale-like clay layer below the sand. This material was easily fractured when removed from the soil mass but should be relatively impermeable if left undisturbed. The entire cut was approximately 6.1m (20 ft) in depth with the fly ash filled to almost the total height.

The third area is the sanitary landfill located in the peninsula of high elevation formed by a bend in the New River. This area has been called the Horseshoe site. It is presently used as a landfill for conventional refuse (garbage, paper, cans, plastics, etc). Refuse is placed using sloped cells in the direction of the long axis of a 91.4m (300 ft) trench. A crawler type tractor is used to move the refuse and soil and for compaction. The exposed trench was approximately 91.4m (300 ft) long, 7.6m (25 ft) wide and 6.1m (20 ft) deep.

The soil characteristics of this site are similar to that in the flyash landfill area. The general color of the soil is rust red (similar to most excavated soil in the area). An examination of the westerly wall of the trench showed the following soil characteristics:

- 0-0.61 m (0-2 ft) - Gray to brown top soil
- 0.61-4.3 m (2-14 ft) - Dense red clay; the densest clay is in the center of this layer, the low portion of the layer is a sandy clay. The surface of the clay exposed to the sun was extremely hard.
- 4.3-6.1 m (14-20 ft) - Clean fine sand, the entire bottom of the trench also consisted of this fine sand, it appeared to be fairly permeable material.

Below the sand layer, there appeared to be the remaining sand and gravel of an old river bed. The soil had the smooth characteristics of a water washed shoreline or bottom material and was quite permeable. Below this layer was a sandy-clay which appeared to hold moisture quite well. However, this layer seemed also quite permeable.

The soil characteristics appeared to be fairly consistent for the entire length of the trench. At the north end of the trench, where the bottom grade blended with the surrounding topography, only the clay layer and top soil were exposed. There were very few rocks and boulders evident in the side walls of the trench. It was assumed that bedrock existed not too far beneath the sandy-clay layer.

Soil samples were collected from the third site, the sanitary landfill, since the possibility still existed to dispose of the NC sludge there. Two types of soil samples were collected. The underlying soil collected was composed of samples from the sandy soil layer. Topsoil samples were collected away from the trench. The first 6.1 - 7.6 cm (2-3 in.) of sod were removed prior to sample collection. All samples were collected in such a manner as to maximize the area represented. Photographs of the sampling sites and trench area are included in the Appendix.

After collection, soil samples were shipped to Envirex in metal drums. Two drums of underlying soil and two drums of topsoil were received.

Sludge Receipt

There was significant delay involved in receipt of the NC lime sludge samples from Radford. Problems associated with shipment of a potentially explosive material required that special analyses and clearances be obtained.

When the sludge did arrive, inspection of the containers indicated that there was insufficient sludge to fill all the columns. Discussion with the project officer indicated that more sludge would be shipped. Another problem existed

with respect to the age of the sludge. This material had been stored in plastic containers in drums for long periods of time (up to 1 year). The liquid had separated from the vacuum filter cake and when the sludge arrived this liquid was covering the solid surface. Therefore, the sludge had to be mixed to form a homogeneous mixture prior to being loaded into the columns. An industrial type Waring blender was used to perform this task. The final mixing and analyses were then delayed until both of the sludge samples had arrived at ESD offices.

These conditions of the sludge caused some initial concern, since there was a question if this material allowed an accurate evaluation of the landfill feasibility. The blending of the sludge did change the appearance from a filter cake material to a thick paste, although the solids content was not significantly affected. However, since the sludge would be compacted in a landfill situation, the composition was anticipated to approach this consistency during the disposal procedure. Therefore, this necessary step should not adversely affect the study results.

Similarly the age of the sludge was of concern. Since the sludge was at least one year old when received, the initial conditions were not necessarily the same as would occur during actual operation. A complete set of initial analyses were performed to set the initial conditions for the study. Samples of sludge were also checked periodically to allow an estimate of concentration change over time. The results indicated that the rate of change was significantly less when the sludge was not being washed by leaching fluid. (This information will be discussed in more detail later in this Section).

Procedure for Filling the Columns

The columns were filled using a sequential procedure to insure as much uniformity as possible throughout all columns. The graded gravel and torpedo sand were placed in the columns. This underdrain was allowed to set prior to further material addition, so that natural settling would occur. The underlying sandy soil was mixed by placing the contents of the shipping drums into a pile on the floor. Rocks greater than 2.54cm (1 in) in diameter were removed since placement of these materials in 15.2cm (6 in) diameter columns would have created unnatural flow conditions. Removal of large rocks from soil samples is commonly performed in column studies. After the soil was mixed and sorted, it was placed into the columns in approximately 15.2cm (6 in) layers, then tamped prior to more soil addition. One layer was placed in all columns, the soil tamped and then the next layer was added. All columns contained 1.37m (4.5 ft) of sandy underlying soil.

After the second shipment of sludge arrived at ESD offices, the sludge and sludge/soil layers were added. After the sludges were blended in the large Waring blender, samples were removed for analysis. Part was used to fill columns and the remainder was mixed with underlying soil. Even with the second shipment of sludge, there was an insufficient amount to allow all columns to be filled to the previously specified amounts. Therefore the 1.83m (6 ft) sludge-only control columns were eliminated and the depth of the sludge and the sludge/soil layers in the 3.66m (12 ft) columns was reduced.

The sludge/soil mixture was then prepared by manually mixing approximately equal volumes of sludge and sandy soil. A photograph of this procedure is included in the Appendix. After the mixture was prepared, samples were removed for analyses and the columns were filled. Radford topsoil was then placed as the top layer in all of the 12 columns.

As indicated, there were changes in the proposed procedure due to small amounts of sludge available for the study. These changes are outlined in Table 2. However, the previously described dosing procedure remained the same. The volumes representing rainfall infiltration rates of 2.54cm, 5.1 cm, 7.6 cm (1, 2 and 3 in.) per month were utilized in the study. A general set-up for the columns is shown in Figure 2.

TABLE 2. COLUMN CONSTRUCTION CHANGES.

Column no.		Column type	
Old	New	Old	New
1	1	Layered: $4\frac{1}{2}$ ft sludge $4\frac{1}{2}$ ft soil	Layered: $3\frac{3}{4}$ ft sludge $4\frac{1}{2}$ ft soil
2	2	Layered: $4\frac{1}{2}$ ft sludge $4\frac{1}{2}$ ft soil	Layered: $3\frac{3}{4}$ ft sludge $4\frac{1}{2}$ ft soil
3	3	Layered: $4\frac{1}{2}$ ft sludge $4\frac{1}{2}$ ft soil	Layered: $3\frac{3}{4}$ ft sludge $4\frac{1}{2}$ ft soil
4	-	$4\frac{1}{2}$ ft sludge only	---
5	-	$4\frac{1}{2}$ ft sludge only	---
6	-	$4\frac{1}{2}$ ft sludge only	---
7	5	Soil $4\frac{1}{2}$ ft underlying soil Only $1\frac{1}{2}$ ft top soil	Soil $4\frac{1}{2}$ ft underlying soil Only $1\frac{1}{2}$ ft top soil
8	7	Soil $4\frac{1}{2}$ ft underlying soil Only $1\frac{1}{2}$ ft top soil	Soil $4\frac{1}{2}$ ft underlying soil Only $1\frac{1}{2}$ ft top soil
9	11	Soil $4\frac{1}{2}$ ft underlying soil Only $1\frac{1}{2}$ ft top soil	Soil $4\frac{1}{2}$ ft underlying soil Only $1\frac{1}{2}$ ft top soil
10	8	Layered: $4\frac{1}{2}$ ft sludge/soil $4\frac{1}{2}$ ft soil	Layered: 4 ft sludge/soil $4\frac{1}{2}$ ft soil
11	9	Layered: $4\frac{1}{2}$ ft sludge/soil $4\frac{1}{2}$ ft soil	Layered: 4 ft sludge/soil $4\frac{1}{2}$ ft soil
12	10	Layered: $4\frac{1}{2}$ ft sludge/soil $4\frac{1}{2}$ ft soil	Layered: 4 ft sludge/soil $4\frac{1}{2}$ ft soil

TABLE 2 (continued).

Column no.		Column type	
Old	New	Old	New
13	-	4 $\frac{1}{2}$ ft sludge/soil only	---
14	-	4 $\frac{1}{2}$ ft sludge/soil only	---
15	-	4 $\frac{1}{2}$ ft sludge/soil only	---
16	4	Layered: 4 $\frac{1}{2}$ ft sludge 4 $\frac{1}{2}$ ft soil	Layered: 3 $\frac{3}{4}$ ft sludge 4 $\frac{1}{2}$ ft soil
17	-	4 $\frac{1}{2}$ ft sludge only	---
18	12	Soil 4 $\frac{1}{2}$ ft underlying soil Only 1 $\frac{1}{2}$ ft top soil	Soil 4 $\frac{1}{2}$ ft underlying soil Only 1 $\frac{1}{2}$ ft top soil
19	6	Layered: 4 $\frac{1}{2}$ ft sludge/soil 4 $\frac{1}{2}$ ft soil	Layered: 4 ft sludge/soil 4 $\frac{1}{2}$ ft soil
20	-	4 $\frac{1}{2}$ ft sludge/soil only	---

$$m = 0.305 \times \text{ft}$$

Initial Sludge and Soil Analyses

Analyses of the soils and sludges were performed to establish baseline conditions for the study. Rainwater analyses were also performed to establish background conditions. The results are presented in Table 3.

The data presented for nitrate/nitrite and TOC values are the best approximation of the initial concentrations. Because of analytical problems encountered later in the study, the analyses performed on the substrates prior to placement in the column are not considered as accurate as later modified analyses performed on refrigerated, stored sludge and sludge/soil samples. It is felt that these numbers are a better approximation of initial concentrations since the known interferences and problems have been accounted for.

The results indicate that the underlying soil does not provide extensive buffering capacity and does not contribute a significant volatile solids fraction to the substrate. This could indicate that the soil may not reduce the pH of the leachate. The soil was quite dry with only a low nitrogen content and little organic material.

The initial concentrations of nitrate/nitrite in the sludge were significant. This was attributed both to the amount of nitrate entrained in the dewatered sludge and the continuing degradation of NC. Because of the high concentrations, the entrained fraction was felt to contribute the most material.

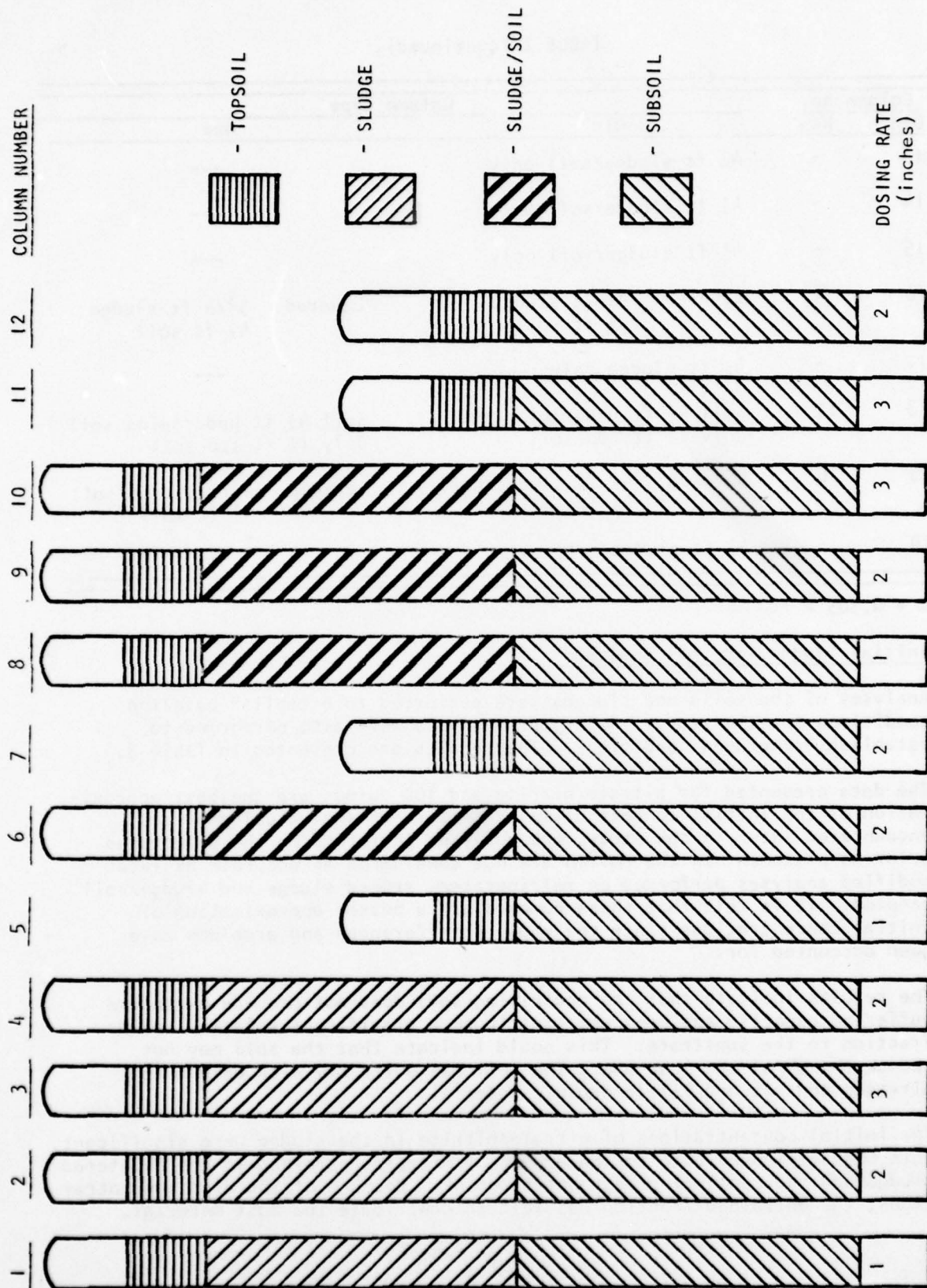


Figure 2. Schematic of column set-up.

TABLE 3. INITIAL ANALYSIS OF NC LIME SUBSTRATE.

Analyte	Units	UNDERLYING				
		Soil	Sludge	Soil/sludge	Rainwater	
Total solids	(TS)	%	89.6	38.1	60.5	-
Total volatile solids	(TVS)	%	2.5	26.8	9.5	-
Moisture		%	10.4	61.9	39.5	-
Ammonia	(NH ₃ -N)	mg/kg (dry wt.)	2	228	117	0.6 mg/l
Kjeldahl nitrogen	(TKN-N)	mg/kg (dry wt.)	67	1550	790	1.1 mg/l
Nitrate/nitrite	(NO ₂ -NO ₃ -N*)	mg/kg (dry wt.)	6.4	23.8x10 ³	7.6x10 ³	0.95 mg/l
Cyanide	(CN)	mg/kg (dry wt.)	<1	8	-	<0.1
Organic nitrate	(Org-NO ₃ -N)	mg/kg (dry wt.)	<1.0	699	202	<1.0
pH		-	5.0	11.9	11.9	7.3
Total organic carbon	(TOC*)	mg/kg (dry wt.)	45	62,700	22,300	12
Total inorganic carbon	(TIC*)	mg/kg (dry wt.)	45	73,380	25,540	16
Density		g/cm ³ (wet)	2.14	1.21	1.64	-

*Best approximation of initial values.

Other nitrogen compounds were also present in relatively high concentrations, due to the continuing NC degradation. Only a small amount of cyanide was present initially.

The sludge and soil were mixed together on a 1:1 volume basis, so the weight fractions of constituents were not reduced in half, especially if the moisture content was considered. However, there were significant decreases in concentration due to the mixing procedures. The consistency of this material was also affected, since the viscosity of the "pasty sludge" was increased. Nitrogen contributions from the soil were quite small compared to the amounts contributed by the sludges.

In order to determine the general accuracy of the analyses, a comparison was made between the assay results printed on the shipping container and the results from the initial testing. The assay results were reported as 30% inerts, 60% water and 10% nitrocellulose. After calculations, it was determined that 73-77% of the available nitrogen was accounted for depending on the degree of nitration. A carbon balance showed recoveries of 123-130% which indicated that the inert constituents were contributing carbon to the system. These calculations did indicate that the analytical procedures were providing results which were reasonable approximations of other techniques.

Leachate Analyses

It was anticipated that the high concentrations of soluble nitrate/nitrite in the sludge would adversely affect the leachate quality. In order to more closely monitor their impact, it was decided to collect small discrete samples at short time intervals within the composite period. These samples would then be monitored for nitrate/nitrite, TOC, ammonia and pH to establish variations in leachate characteristics which could occur over shorter times. The collection and analysis of discrete samples would also provide an indication of sudden changes in leachate quality, so that additional analyses could be performed if needed.

Dosing volumes representing rainfall infiltration rates of 2.54cm, 5.1cm and 7.6cm (1, 2 3 in.) per month were utilized in the study. Table 4 summarizes the dosing schedule followed. The columns were dosed twice per week with the appropriate volume of rainwater. As a result of the slow leaching rate encountered with columns 9 and 10, a standing head was established in both columns in January 1977 and maintained by twice per week dosing through the remainder of the study.

Three of the columns were operated in an "inundated condition". This involved raising the outlet of the leachate collection tube to a level even to the substrate layer. In this way, the impact of a raised groundwater level on leachate quality could be established.

Leachate samples were collected and composited on a daily basis or whenever sufficient volume had collected in the flask. Once the columns had reached "steady-state", leachate collection was performed three times per week. Samples were split between discrete and composite volumes, with the

composite amount further divided between an acidified and non-acidified fraction. The following guidelines were followed for the composite and discrete sample collection procedure.

1. Samples were composited if 25 mls or more of leachate had collected.
2. Volume and pH were measured for all samples being composited.
3. Discrete samples were collected for all columns when a volume of 50 mls or more was available or if the investigator determined that discrete analyses were desirable.
4. 20% of the volume for composite was split into an acidified sample (acidification was done by addition of 0.1 mls of 1N H_2SO_4 per every 10 mls of samples).
5. The remaining 80% of the volume was placed into a refrigerated only composite.

TABLE 4. DOSING SCHEDULE LYSIMETER COLUMNS.

Column number	Column height	Column type	Dosing rate
1	12 ft	Sludge - gravity flow	1"/month
2	12 ft	Sludge - gravity flow	2"/month
3	12 ft	Sludge - gravity flow	3"/month
4	12 ft	Sludge - partially inundated	2"/month
5	6 ft	Soil only - gravity flow	1"/month
6	12 ft	Sludge/soil - partially inundated	2"/month
7	6 ft	Soil only - gravity flow	2"/month
8	12 ft	Sludge/soil - gravity flow	1"/month
9	12 ft	Sludge/soil - gravity flow	2"/month
10	12 ft	Sludge/soil - gravity flow	3"/month
11	6 ft	Soil only - gravity flow	3"/month
12	6 ft	Soil only - partially inundated	2"/month

m = 0.305 x ft

cm = 2.54 x inches

Initially, the composite period was set at 2 weeks or 10 working day intervals to allow collection of more information during periods of rapid changes. However, at times, sufficient volumes of sample were not available to perform all analyses. Therefore, the prescribed analyses were assigned a priority for performance. The analyses to be performed on the various samples are listed in order of priority in Table 5.

After the concentrations of the various parameters had leveled off, the composite period was extended to 4 weeks or 20 working days. This allowed collection of larger sample volumes which improved detection limits and yet did not adversely affect the overall study objectives. The analyses chosen to be monitored were initially identified from the previous literature review. The preliminary results indicated that the degradation products were much more complex than originally anticipated. As a result, additional analyses were included at this point and throughout the study. These analyses are listed in Table 6.

Problems were encountered in obtaining leachate from the two 3.66m (12 ft) inundated columns 4 and 6. Since they had not produced leachate following normal dosing procedures, they were placed under 15.2cm (6 in.) of standing water on April 1, 1977 under 30.5cm (12 in.) on April 19, 1977 and under 18 in. on May 16, 1977. Still no leachate had been produced. In June 1977 the two columns were pressurized using air initially to 1.15 atm (2 psi), then to 1.24 atm (5 psi) in July 1977, and finally to 1.5 atm (7 psi) in August 1977 to try to force leachate production. Column 4 started producing small volumes of leachate intermittently from August to December 1977. Column 6 never produced a leachate.

ANALYTICAL INTERFERENCE EVALUATION AND COMPENSATION

During the study, an interference was noted which affected analytical results from sludge column leachate samples. The interferent gave trailing peaks on the inorganic channel of the Beckman TOC analyzer and interfered with ammonia analyses on both the Technicon AAII module and the ammonia ion specific probe. Several approaches were used to begin the identification of the unknown compound causing analytical problems.

Identification of the Interferent

The first approach was to measure for residual chlorine by the iodometric technique. The result was an apparent chlorine content of 10^4 magnitude (column #1). Subsequent spot and flame tests, however, failed to confirm the presence of chlorine. There was also no record of additives in the sludge's history which would produce such a high concentration of chlorine. Other materials such as cyanide or thiocyanate which may have originated as a result of alkaline degradation of nitrocellulose were not found in sufficiently high concentrations to cause these results.

At this point it was known that a constituent or constituents in the leachate from columns containing sludge could cause interferences to the TOC, and $\text{NH}_3\text{-N}$ analysis, and upon acidification with H_2SO_4 (10% V/V) would yield a white precipitate (2.8% TVS content) and evolve brownish-

TABLE 5. ANALYSES TO BE PERFORMED ON COLLECTED LEACHATE, EARLY PHASE.

Discrete samples	1. Nitrate/nitrite.* 2. Total organic carbon.* 3. Ammonia.* 4. pH.
Acidified composite samples	1. Nitrate/nitrite. 2. Total carbon. 3. Ammonia. 4. Total kjeldahl nitrogen. 5. Chemical oxygen demand.
Refrigerated composite samples	1. Organic nitrate. 2. Alaklinity. 3. pH. 4. Conductivity. 5. Cyanide (periodically). 6. Total solids. 7. Total volatile solids. 8. Total dissolved solids.

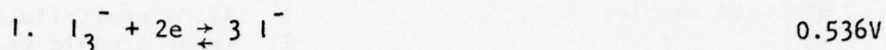
*After acidification with sulfuric acid.

TABLE 6. ANALYSES PERFORMED ON COLLECTED LEACHATE, LATER PHASE.

Discrete samples (after acidification with sulfuric acid)	1. Nitrate/nitrite. 2. Total carbon.
Acidified composite samples	1. Nitrate/nitrite. 2. Ammonia. 3. Total kjeldahl nitrogen. 4. Total carbon. 5. Chemical oxygen demand.
Refrigerated composite samples	1. Organic nitrate. 2. Alkalinity. 3. pH. 4. Conductivity. 5. Thiocyanate. 6. Total solids. 7. Total dissolved solids. 8. Total volatile solids. 9. Dissolved volatile solids. *10. Total cyanide. *11. Biochemical oxygen demand *12. Total coliforms.

*Infrequent analysis.

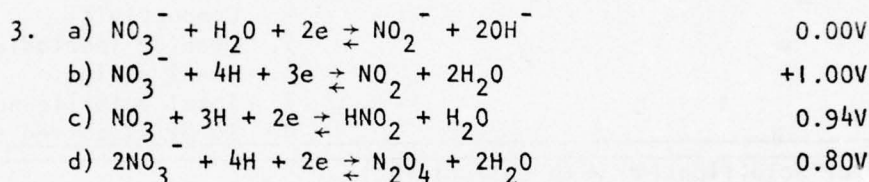
yellow pungent fumes. An analytical approach based on standard redox potentials was then chosen as the method for isolating the possible contaminant. The work with the iodometric chlorine test indicated the oxidant possessed a redox potential $> 0.536V$ (eq. 1.).



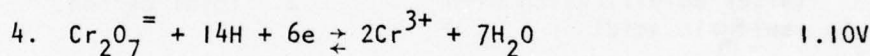
The ability to oxidize Ce(III) to Ce(IV) (eq. 2) in a 1M H_2SO_4 system using ferroin as an indicator would indicate the presence of some of the stronger oxidants, i.e. $> 1.61V$ such as ozone, persulfate or peroxide.



The constituents in the leachate from column 1 were unable to do this. Controls run with fresh persulfate successfully oxidized the cerrous ion to the ceric form. The potentials of the most abundant ion in the leachate i.e. the nitrate (or nitrite) ion were then investigated (eq. 3a-d).



The reduction of the nitrate to the nitrite ion was a poor candidate but reactions 3b through 3d had positive enough potentials to interfere in the iodometric titration. However, the formal potentials were below those of the conversion of Cr(III) to Cr(VI) in eq. 4. The formal potential



of this system allowed differentiation between the nitrate and the chlorine molecules as the interferant, (eq. 5). Cr(III) oxide was the



reduced chromium source. The leachate-chrome (III) system was made in 1M H_2SO_4 . The chlorine-chrome control was adjusted for a 10 fold excess of the OCl^- group using 15% Na OCL and made acidic to an 1M concentration, thus liberating Cl_2 gas. Both systems were covered and placed on a steam bath for 72 hours. At the end of the 72 hours 86% of the Cr(III) had been converted to Cr(VI) (measured by the diphenyl-carbohydrazide colorimetric technique) in the chlorine system while in the leachate system $<1\%$ Cr(VI) had been formed. These tests are far from conclusive. Measurement of formal potentials in complex systems can be masked by many side reactions, and although the thermodynamics of a given redox reaction is favorable, the kinetics may not be. However, these data do suggest that the interferant in the leachate is the nitrate ion.

This is further implied by the fact that a control made to 10,000 mg/l NO_3^- caused tailing peaks on the TIC channel of the Beckman TOC analyzer and the control liberated brownish-yellow pungent fumes upon acidification with H_2SO_4 (note eq. 3b and 3d). (Note: the white precipitate composition from the leachate is unknown).

Impact on Analyses

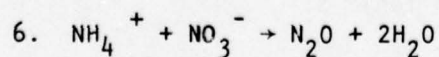
Assuming the nitrate ion to be the problem, a series of analysis were performed to evaluate its influence on the TOC, COD, and TKN analysis. The results of these tests are given in Table 7. There was no detectable interference in the COD test. The TOC showed lower recoveries for high concentrations of the nitrate ion. This can be attributed to an exaggerated TIC response. The controls were made from deionized water containing less than 3 mg/l CO_2 and yet the injected samples gave a TC of 102 and a TIC of 85 for the 10,000 mg/l $\text{NO}_3\text{-N}$ control and a TC of 21 with a TIC of 14 for the 1,000 mg/l control.

These TIC peaks showed the tailing effect so characteristic of the NC-lime leachate samples. The high concentrations of nitrate/nitrite in the leachate had been causing a positive interference in the TIC response resulting in lower TOC values than were actually present. It is theorized that nitrous oxide was being formed which was read as CO_2 by the infrared analyzer. To overcome this interference the leachate samples were acidified and only total carbon was measured, which should more closely approximate the actual TOC values.

TABLE 7. INTERFERENT STUDY.

Analysis	$\text{NO}_3\text{-N}$ concentration, mg/l	Analyte added	Recovered	% Recovery
COD	10,000	266	247	93
TOC	10,000	100	17	17
	1,000	20	7	35
	200	80	75	94
TKN	10,000	0	<0.1	-
	200	20	5.5	28
	200	100	76.0	76
	200	200	135	68

TKN Impacts - The nitrate ion caused a negative interference in the TKN analysis. The results in Table 7 are in agreement with those of Schluter ("Nitrate Interference in TKN Determinations and its Removal by Anion Exchange Resins", EPA-600/7-77-017, Feb. 1977) (21). One proposed reaction causing the interference is given in equation 6, although the reaction is suspected to be more complex.



This reaction indicates that water inhibits the interference. Therefore, as the water is driven off in the TKN digestion, the reaction proceeds to the right. Schlueter recommends the use of anionic exchange resins to remove the nitrate ion. This method requires that the reacted resin then be removed by filtration. This would also remove any particulate organic nitrogen causing a negative error. While this may be a general procedural problem, in the NC-lime leachate sample, the suspended solids concentration were quite low and did not pose a problem. This method of nitrate removal was further evaluated.

Our initial step was to determine if the NC-lime leachate would cause a TKN interference. A TKN standard was spiked with NC-lime column leachate on a two to one and on a one to one TKN to nitrate nitrogen basis and the TKN determined. The leachate caused a negative interference on the TKN analyses, resulting in only 71% recovery.

The next approach was to test the use of an anion exchange resin to remove the nitrate prior to the TKN digestion. The specified anion exchange resin, Ionac A-540, was obtained. The capacity of the resin to remove nitrate from solution was determined experimentally. It was found that to remove one milligram of nitrate nitrogen from solution requires approximately seven grams of resin. The procedure developed for using the anion exchange resin to denitrify a sample is as follows:

1. Based on nitrate levels in the sample, determine the amount of resin necessary for denitrification.
2. Prerinse the appropriate amount of resin to be used on the sample and an equal amount of resin for a blank with deionized water to remove TKN solubles. (400 mls of deionized water to 15 grams resin washed).
3. Filter rinse water from sample resin and resin blank under low vacuum.
4. Transfer resin to 50 milliliters of sample, stir slowly on magnetic stirrer for 15 minutes to allow denitrification of sample. Transfer resin blank to 50 milliliters of deionized water and treat in same manner as sample.
5. Under low vacuum, filter the original 50 milliliters of sample from the resin. Do the same for the resin blank.
6. Now that the sample is denitrified, take it and the blank through the regular TKN procedure (digestion, distillation, and titration). Subtract the resin blank from the sample in the calculations.

The validity of this procedure was tested on a TKN solution (4-Aminoantipyrine) spiked with nitrate at ten times the TKN level. Replicates were analyzed, the results are given in Table 8.

TABLE 8. NITRATE INTERFERENCE IN TKN ANALYSIS STUDY.

Sample	Recovered TKN, mg/l	% Recovery
TKN solution.	128	
	126	
Ave.	127	-
Nitrate spiked TKN solution.	2	
	3	
	3	
Ave.	3	2
Nitrate spiked TKN solution after denitrification by anion exchange.	137	
	129	
	146	
Ave.	137	108

A 98% loss of TKN occurred in the nitrate spiked TKN solution. However, the nitrate interference could be successfully removed by the denitrification procedure, allowing good TKN recovery.

Leachate samples from the six columns with high nitrate levels were then analyzed both with and without preliminary denitrification. Results are given in Table 9. TKN levels were found to be higher when the sample was denitrified prior to analysis. Most of the problems encountered in this investigation were due to the high nitrate levels in the NC-lime leachate. Large amounts of resin were required for denitration. This made the use of small sample aliquots mandatory, which may have reduced recoveries. Tests in which replicates were analyzed showed the technique to be precise for most samples. However, due to difficulties inherent in the use of small sample volumes there is quite a variation in results.

Ammonia Analyses - There were also some problems encountered with ammonia analysis. The high concentration of nitrate/nitrite in the NC lime leachate samples caused a positive interference in ammonia analysis by Technicon AA II module. Since the ammonia levels were relatively low, this effect could not be compensated for with additional dilution. Problems also occurred when analyzing ammonia with the ammonia ion specific probe due to the high dissolved solids in the leachate samples. A standard ammonia distillation into boric acid followed by probe analysis successfully removed interferences in the ammonia analyses. The procedure did require more sample volume so individual samples were analyzed only once every two weeks.

COLUMN DISASSEMBLY AND RESIDUAL ANALYSES

Column Disassembly

The last leachates were collected and the columns disassembled for analysis

TABLE 9. NITRATE INTERFERENCE IN TKN ANALYSIS OF LEACHATE.

Column	Sample Date	TKN, mg/l	
		With denitrification	Without denitrification
1	December 9, 1977- January 16, 1978	56	<70
1	January 16, 1978- February 20, 1978	126	-
2	November 4, 1979- December 19, 1977	168	<70
2	December 19, 1977- January 24, 1978	182	-
2	January 24, 1978- February 28, 1978	98	-
3	December 9, 1977- January 16, 1978	378	<70
3	January 16, 1978- February 20, 1978	126	-
8	November 18, 1977- December 23, 1977	252	<70
8	December 23, 1977- January 30, 1978	392	-
8	January 30, 1978- February 6, 1978	182	-
9	November 18, 1977- December 23, 1977	140	<70
9	December 23, 1977- January 30, 1978	392	-
9	January 30, 1977- February 6, 1978	98	-
10	November 11, 1977- December 16, 1977	112	<70
10	December 16, 1977- January 23, 1978	532	-
10	January 23, 1978- February 27, 1978	112	-

approximately 22 months after the dosing began. To accomplish this the columns were removed from their wall supports and lowered to a horizontal position on the laboratory floor. Approximately 1/4 of the circumference of the PVC pipe was removed by 2 lengthwise cuts made with a powersaw exposing the sludge and soil layers in each column. Profile measurements were made and subsamples for analysis were then taken at the depths shown in Table 10. The remaining sludge or sludge/soil from each column was transferred to containers and refrigerated. Topsoil and subsoil was returned to the shipping drums. Pictures of the operation are included in the Appendix.

Residual Analyses

The analyses performed on the residual sludge and soil in the disassembled columns are listed in Table II.

TABLE II. ANALYSES PERFORMED ON DISASSEMBLED COLUMNS.

Nitrate/nitrite
Organic nitrate
Total cyanide
Thiocyanate
Total organic carbon
pH
Total solids
Total volatile solids
Density*
Oxidation-reduction potential*

*Not performed on all samples.

These analyses were performed on the disassembled columns samples to characterize the extent of sludge degradation at the end of the study and to gain information on the vertical movement and fate of sludge degradation products.

For most parameters, standard procedures or the modified procedures previously outlined were used in the analyses. However, the cyanide technique required some modification.

The NC-lime sludge and leachate samples were analyzed for total cyanide according to the method outlined in Standard Methods 14th edition - Total Cyanide after Distillation (413B) followed by the Titrimetric Method (413C) to determine CN concentration. In this method cyanide complexes in the sample are converted to hydrogen cyanide gas and absorbed into sodium hydroxide solution. The amount of cyanide absorbed is analyzed titrimetrically. Magnesium chloride was added to the distillation to eliminate thiocyanate interference.

Distillation gives quantitative recovery of even the refractory cyanide complexes. Several tests were performed to test recovery of cyanide from

TABLE 10. COLUMN PROFILES AT DISASSEMBLY AND DEPTHS AT WHICH SUBSAMPLES WERE TAKEN.

Column	Topsoil	Sludge	Underlying soil
#1 Profile	0-14"	14-57"	57-107"
Subsamples	7"	15, 25, 35, 45, 55"	69, 95"
#2 Profile	0-13"	13-54"	54-112"
Subsamples	7"	14, 24, 34, 44, 52"	66, 100"
#3 Profile	0-15"	15-56"	56-106"
Subsamples	-	17, 27, 37, 47, 55"	68, 94"
#4 Profile	0-15"	15-55"	55-105"
Subsamples	-	17, 27, 37, 47, 53"	67, 93"
#5 Profile	0-15"	-	15- 72"
Subsamples	7"		27, 60"
#6* Profile	0-14"	14-60"	60-114"
Subsamples	-	16, 26, 36, 46, 58"	72, 102"
#7 Profile	0-15"	-	15- 77"
Subsamples	8"		29, 65"
#8* Profile	0-15"	15-63"	63-119"
Subsamples	7"	17, 27, 37, 47, 61"	75, 107"
#9* Profile	0-12"	12-60"	60-122"
Subsamples	6"	14, 24, 34, 44, 58"	72, 110"
#10* Profile	0-16"	16-67"	67-129"
Subsamples	8"	18, 28, 38, 48, 58, 65"	79, 117"
#11 Profile	0-18"	-	18- 76"
Subsamples	9"		30, 64
#12 Profile	0-18"	-	18- 75"
Subsamples	9"		29, 63

*Columns containing sludge/soil mixture.
cm = inches x 2.54

NC-lime sludge samples. Replicates were distilled for one and two-hour periods. As shown in Table 12, a two-hour distillation time recovered approximately 30% more cyanide than a one-hour distillation. The samples distilled for two hours showed very good replication, which tends to indicate a more complete recovery of total cyanide. Based on this, all NC lime sludge and leachate samples were distilled for two hour periods to allow a more complete recovery of the total cyanide present.

TABLE 12. TOTAL CYANIDE RECOVERED FROM ONE AND TWO HOUR DISTILLATION OF SLUDGE.

Sample	Distillation time	Total CN, mg/kg dry wt.	Average mg/kg dry wt.
Sludge	1 hour	360	339
	1 hour	317	
	2 hours	436	441
	2 hours	445	

As a check on the accuracy of the method, replicates of the sludge were spiked with cyanide standard on a 1 to 1 cyanide in sample to spike basis (Table 13). Recoveries averaged 99%. A leachate sample was then spiked, resulting in a 94% recovery of total cyanide. This indicated that the total cyanide analysis on the NC-lime sludge and leachate samples was not significantly affected by any interference(s) present. It also strengthens the validity of the results obtained using this method for NC-lime total cyanide analysis.

TABLE 13. RECOVERY OF CYANIDE FROM SPIKED SLUDGE AND LEACHATE SAMPLES.

Sample	CN found, average	Actual CN	% Recovery
Sludge	1.17 mg	2.17 mg	99%
Spiked sludge	2.15 mg		
Leachate	3.3 mg	5.3 mg	94%
Spiked leachate	5.0 mg		

RESULTS AND DISCUSSION

The study yielded many interesting results with respect to the sludge characteristics, leachate quality, as well as the degradation of the nitrocellulose fines entrained in the sludge. These results are presented in the remainder of this section.

Low Permeability of the Sludge and Sludge/Soil Systems

One of the most significant results of the study was the finding that both the sludge and the sludge/soil mixtures had quite low permeabilities to leaching water. This became apparent immediately after the study began, since the sludge and sludge/soil columns did not reach field capacity for extended periods of time. The soil control columns operating in the downflow mode produced a leachate within 15 days after the start of high rate dosing, 2.54 cm/day (1"/day). However, the 3.66m (12 ft) study columns did not produce a leachate, and water began to accumulate above the topsoil layer. This accumulation continued so the high rate daily dosing was halted and the water level was monitored. Since there was a standing water head, the columns were, in effect, pressurized by this weight of water standing on the surface and saturating the topsoil layer.

Since it was necessary to obtain a leachate for analyses, further steps were taken to hasten its production. Two of the tall sludge filled columns were pressurized by sealing them and placing metered air pressure onto the column. Effective pressures of 1.148 atm (5' of water head) were utilized. Two days after pressurization, the pressurized sludge column produced a leachate. However, on the next day, an unpressurized sludge column produced a leachate. The pressure on the sludge column was then released and leachate continued to flow by gravity. The remaining gravity flow sludge column and the partially inundated sludge column produced visible leachate later. The time required for these columns to reach field capacity was 30-45 days.

The sludge/soil mixture had an even lower permeability. Pressure to levels of 1.48 atm (15' of water head) remained on the tall column 41 days before a leachate was produced. Soon after, both of the gravity flow columns produced leachates and liquid was visible in the clear tubing on the partially inundated column. These columns required approximately 3 months to reach field capacity.

Throughout the remainder of the study, attempts were made to force a leachate through the sludge and sludge/soil columns operated under partially inundated conditions. These columns were pressurized at 1.48 atm (15' of water head) for up to 12 months. However, in the field, these high pressures would not likely be encountered under natural conditions. A summary of the time needed to reach field capacity and the volume of rainwater added before a leachate was produced is presented in Table 14.

Another indication of the low permeability of these materials is the relationship between the volumes dosed and the volumes leached for the different columns. These results are presented graphically in Figure 3. The extremely low permeability of the sludge/soil mixtures is apparent when the small volume of collected leachate is considered. The sludge itself has the ability to leach, but the amount is not directly proportional to the volume dosed. This can be seen by comparing the volume of leachate collected for columns 11 and 3. The control (Column 11) and the sludge column (Column 3) were both dosed at a rate of 7.62 cm (3"/month), yet there was 25% more leachate collected from the control column. This finding can also be presented by calculating the number of equivalent bed

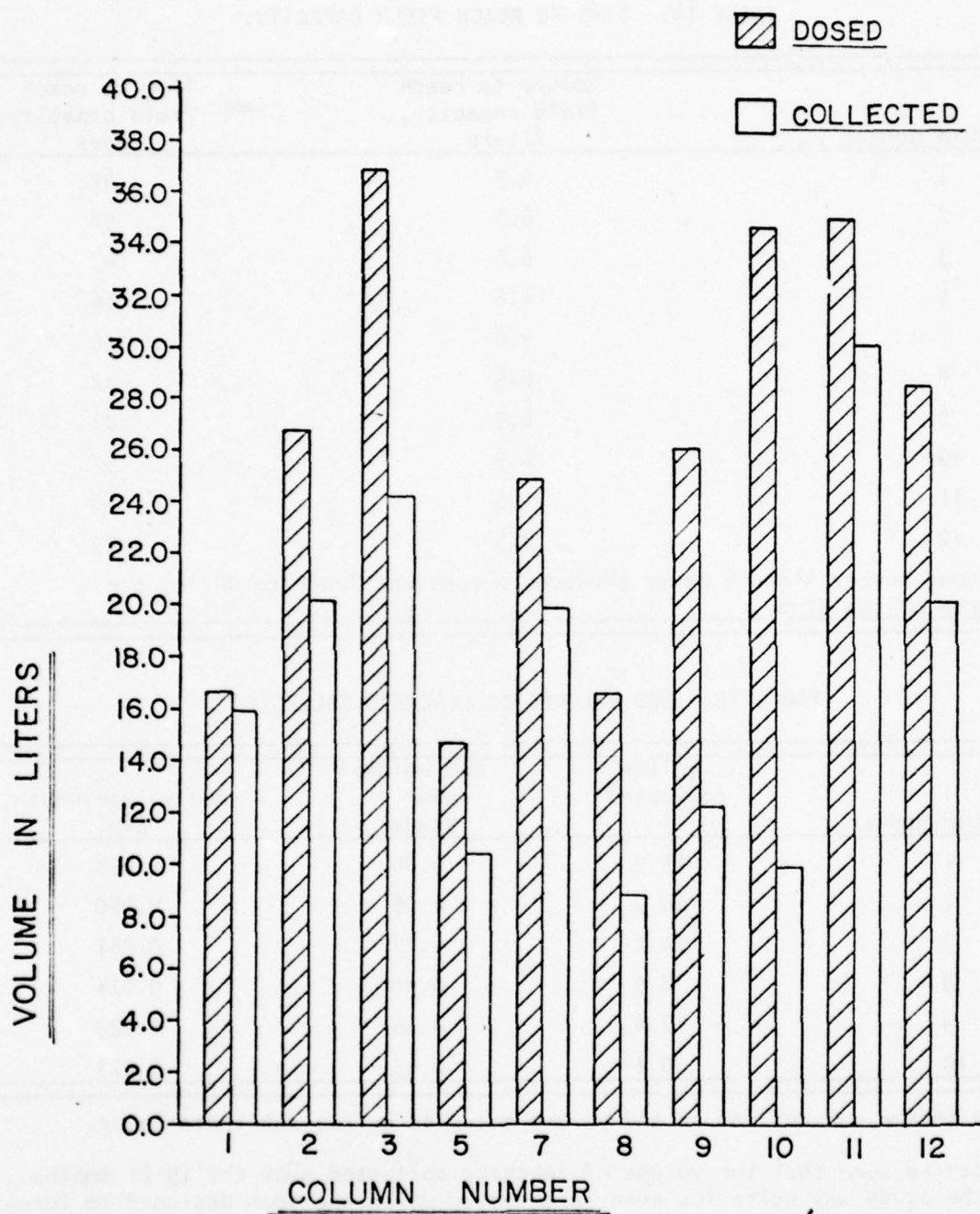


Figure 3. Volumes of liquid dosed and collected by columns.

volumes of leachate produced by the various columns. These are summarized in Table 15.

TABLE 14. TIME TO REACH FIELD CAPACITY.

Column number	Volume to reach field capacity, liters	Time to reach field capacity, days
1	6.5	42
2	6.5	54
3	6.5	43
5	4.6	16
7	4.6	16
8	6.5	82
9	6.5	103
10	6.5	91
11	4.6	16
12	8.3	29

Columns number 4 and 6 never produced a constant leachate during the course of the study.

TABLE 15. BED VOLUMES OF LEACHATE COLLECTED.

Column number	Volume collected, l	Bed volume* over study	Bed volume*/month, avg.
1	15.9	0.80	0.038
2	20.2	1.06	0.050
3	24.2	1.28	0.061
8	8.9	0.40	0.021
9	12.4	0.56	0.029
10	10.1	0.43	0.023

*Bed volume was defined as the volume occupied by the substrate layer.

It can be seen that the volume of leachate collected over the 19-21 months of the study was quite low even in a system which has been designed to force leachate production.

Leachate Quality

The composite and discrete samples were analyzed for the various parameters throughout the duration of the project. The results have been compiled into Tables which are included as the Appendices of this report. There were some significant findings with regard to several parameters which are highlighted in this discussion. In all instances, the control column leachate had low concentrations of all parameters of interest. The contribution of chemical constituents from the soil was quite small.

High Concentrations of Nitrate/Nitrite - Extremely high concentrations of nitrate/nitrite were found in the leachate from the sludge columns. The general trend of nitrate/nitrite concentrations versus time is shown in Figure 4. It can be seen that there was an initial rapid increase in concentrations until peak levels were reached. Then the nitrate/nitrite values leveled off at concentrations of 11-13,000 mg/l $\text{NO}_2\text{-NO}_3\text{-N}$ for the sludge columns and 8-11,000 mg/l $\text{NO}_2\text{NO}_3\text{-N}$ for the sludge/soil systems. Figure 4 also shows the significant decline in nitrate/nitrite concentrations toward the end of the study. This reduction corresponds to the leaching of most of the nitrate/nitrite originally present in the sludge when it was placed in the columns. The decrease is not apparent for column 1 or the sludge/soil systems since the volumes of leachate produced to that date were less than that for columns 2 and 3. However, it is anticipated that these would also follow the same pattern over a longer period of time.

These results are significant since they indicate a potential problem associated with the leachate quality. The high nitrate/nitrite levels can adversely affect ground water quality. Typically, nitrate concentrations are limited to less than 45 mg/l since higher levels can contribute to an illness known as infant methemoglobinemia (22). The fact that the nitrate/nitrite levels decrease when much of the initial nitrate is rinsed through the system is also important since it indicates that previous washing of the sludge could reduce the direct nitrate/nitrite impact on the ground water.

There was a question as to whether the entire amount of nitrate/nitrite being leached could be attributed to the concentrations originally present in the sludge or whether the continued degradation of the nitro-cellulose fines contributed to the nitrate levels. Summation of the nitrate present in the various leachates indicated that for column 3 (high dosed; sludge only) the amounts of nitrate collected exceeded that originally present. This indicated that there was an additional source of nitrate/nitrite, hypothesized to be degradation of the NC.

To confirm this finding, a sludge sample was washed to remove most of the entrained nitrate. Then samples were removed monthly and analyzed for inorganic nitrate/nitrite and organic nitrate to determine if continuing degradation of the NC could increase available inorganic materials. The summarized results of 3 sets of analyses are presented in Table 16. There was a consistent increase in inorganic nitrate/nitrite levels throughout

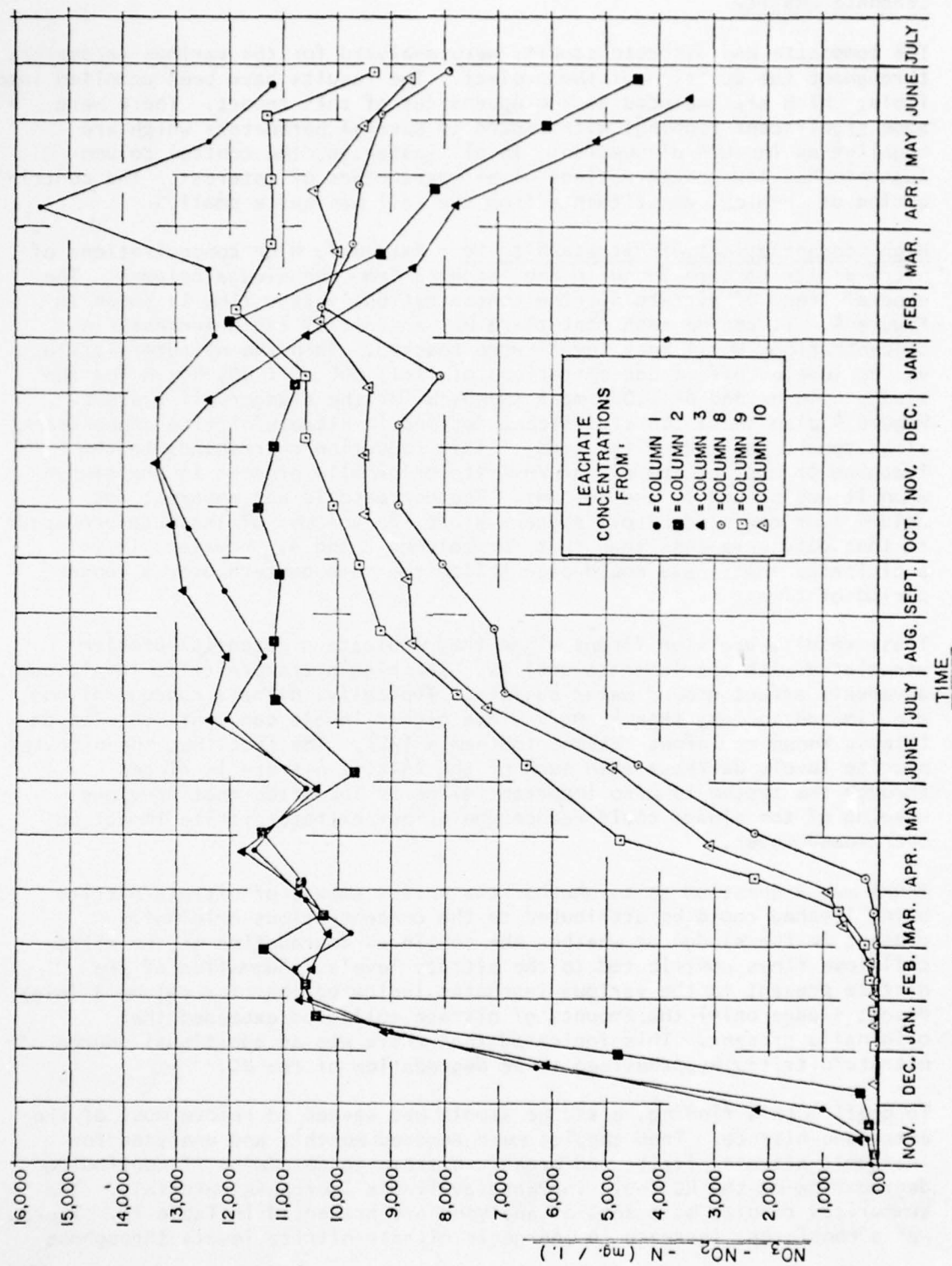


Figure 4. Variation in nitrate/nitrite concentrations with time.

the seven month period. A corresponding decrease in organic nitrate was also noted. These values confirm the fact that the NC continues to degrade in the alkaline environment presented by the lime sludge. The rate is faster if the equilibrium is disturbed by washing.

TABLE 16. SLUDGE DEGRADATION TEST RESULTS.

Time of sample, months	Average inorganic NO ₂ /NO ₃ -N, mg/kg dry wt	Average organic NO ₃ -N, mg/kg dry wt
0	67	702
1	358	456
2	467	495
3	627	364
4	699	454
5	726	324
6	992	267
7	1330	77

Nitrocellulose Fines - Nitrocellulose fines were not leached from the sludge. The analytical results have indicated that there is less than 0.1 mg/l of organic nitrate present in the leachate samples. This finding is significant since prior to the initiation of this study, there was no data which established potential ground water contamination by these fines. The fact that no fines migrated to the leachate during this study indicates that this type of contamination will probably not occur in a full scale disposal site.

Total Organic Carbon - Total organic carbon concentrations followed the same general trend indicated by the nitrate/nitrite system (Figure 5). The increases in concentration were more gradual and did not reach as high a level, but the initial increase, leveling off and eventual decline were evident. Since the NC could degrade into a wide variety of end products which are not identified by a general TOC analyses, it was felt that further quantification would be desirable.

Solids Concentrations - Solids concentrations were also monitored throughout the study. The results of total solids and total volatile solids analyses are presented in Figures 6 and 7. There was a large increase in solids concentrations for columns 1, 2 and 3 during the initial phases of the study. The increases noted for column 8, 9 and 10 were much more gradual

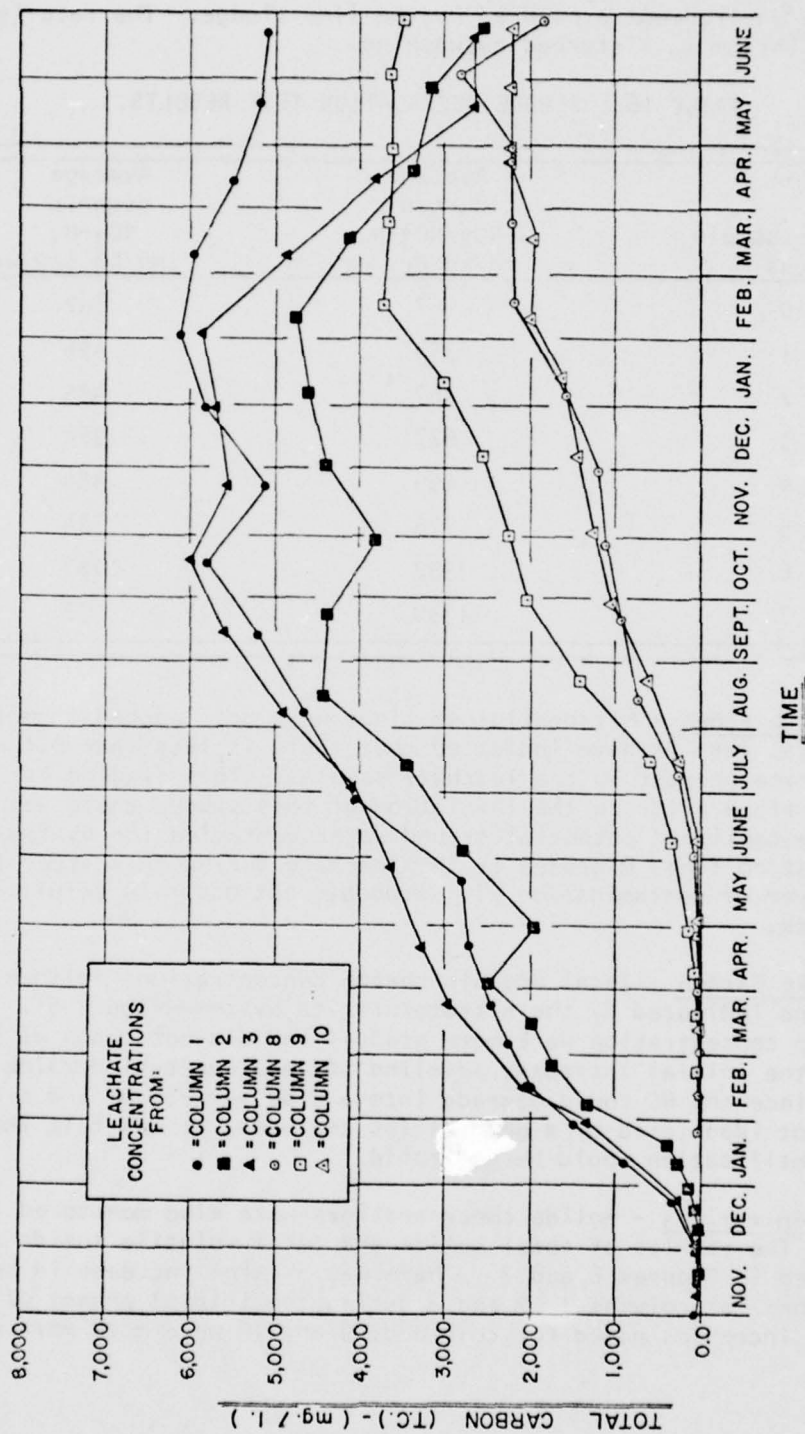


Figure 5. Variation in TOC concentrations with time.

and the concentrations were just leveling off at the time the study was completed. Solids concentrations were high, approximately 8% total solids and there was a significant volatile fraction. Most of the solids were dissolved which was expected, since most particulates were removed by the sandy subsoil layer.

Cyanide Concentrations - The preliminary review of potential degradation products had indicated that there was the chance that cyanide could be formed during alkaline decomposition of the NC. Therefore, leachate samples were analyzed for cyanide content. The results indicated that cyanide concentrations ranged from 3 to 20 mg/l in the leachate samples. The sludge column leachate generally included more cyanide (12-20 mg/l) than the sludge/soil leachate system. Control columns' leachate and rainwater contained less than 0.1 mg/l of total cyanide. The levels of cyanide did vary somewhat with time, however, the range remained the same. It should be noted that the cyanide measured was total cyanide which includes most organic and metallic cyanide complexes. Free cyanide was not present in significant amounts. This more mobile form may have been lost from the system at the neutral pH or was immediately complexed upon formation.

In addition to cyanide itself, thiocyanate (SCN^-) was also present in the leachate. Concentrations as high as 71 mg/l were analyzed in some sludge column leachate samples. The typical range for the sludge system was 40-70 mg/l SCN. The sludge/soil thiocyanate concentrations varied considerably. They were generally lower, with ranges of 3-47 mg/l and the columns with a less volume leached had lower SCN concentrations. The results indicated that both cyanide and thiocyanate were degradation products of the nitrocellulose.

Leachate pH - Another interesting observation involved the pH of the collected leachate samples. Most were neutral, ranging from 6-8 pH units. Since the pH of both the sludge and the sludge/soil was quite high, this result was somewhat surprising. It is surmised that the leachate does become alkaline when moving through the substrate, however, this alkalinity is reduced by the buffering capacity of the soil before the leachate leaves the column. The soil does not have sufficient acidity to noticeably impact the sludge when mixed in the 1:1 ratio, however, the small volumes of leachate produced do seem to be neutralized by the subsoil.

Sludge Characteristics

The sludge and sludge/soil remaining in the columns were analyzed in sections after column disassembly. Several of the resultant parameter concentrations were significantly less than those originally analyzed. The main exception was total cyanide which increased during the period of study. The complete analytical results are presented in the Appendix.

Sludge/Subsoil Interface - The results indicate a clear distinction between the contaminant concentrations in the sludge or sludge/soil and that found in the subsoil in each column. The sandy subsoil appeared to act as a filter immediately at the interface and therefore, protected underlying soil layers from contaminated particulates or solid complexes. The

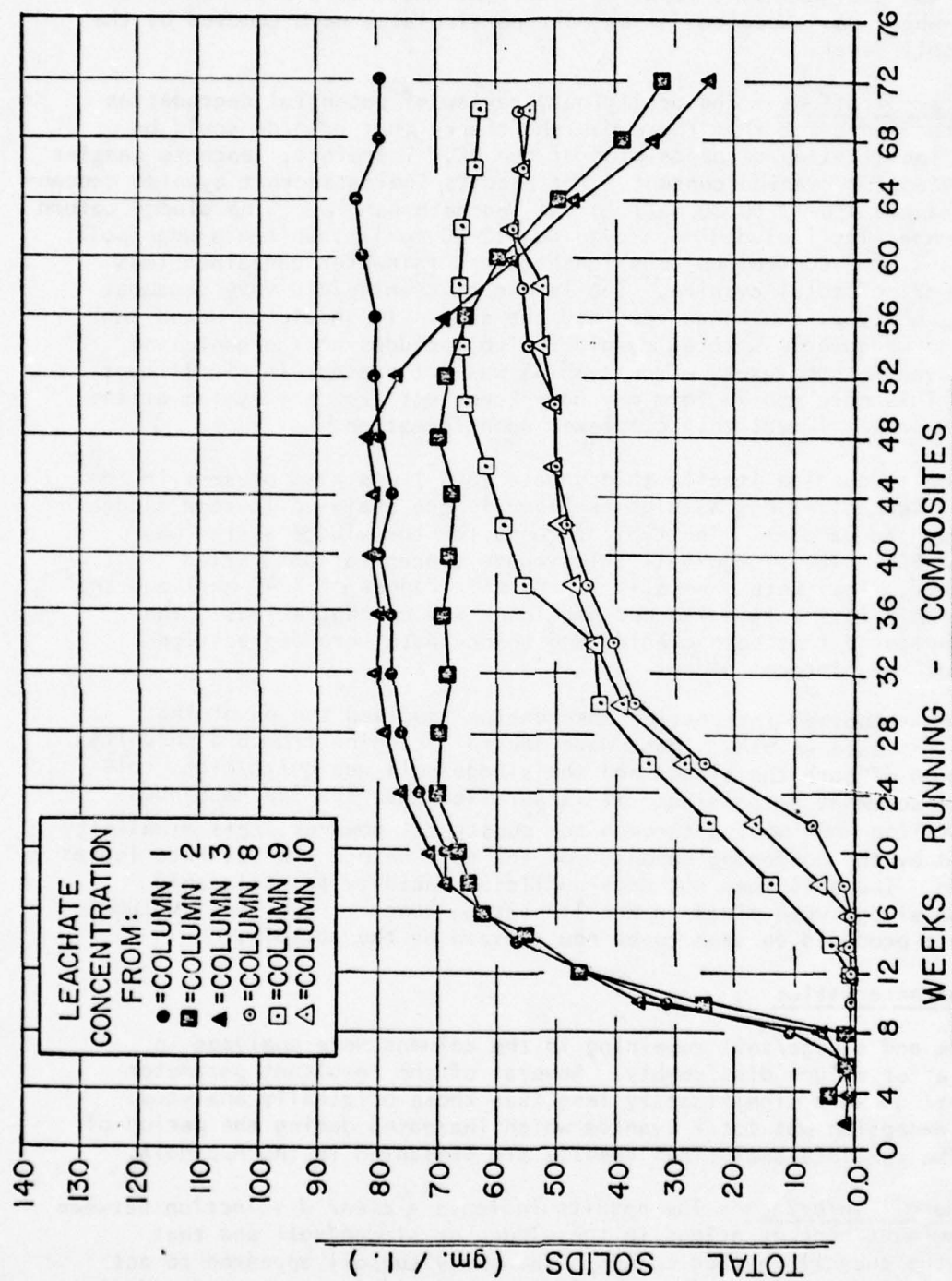


Figure 6. Variation of total solids with time.

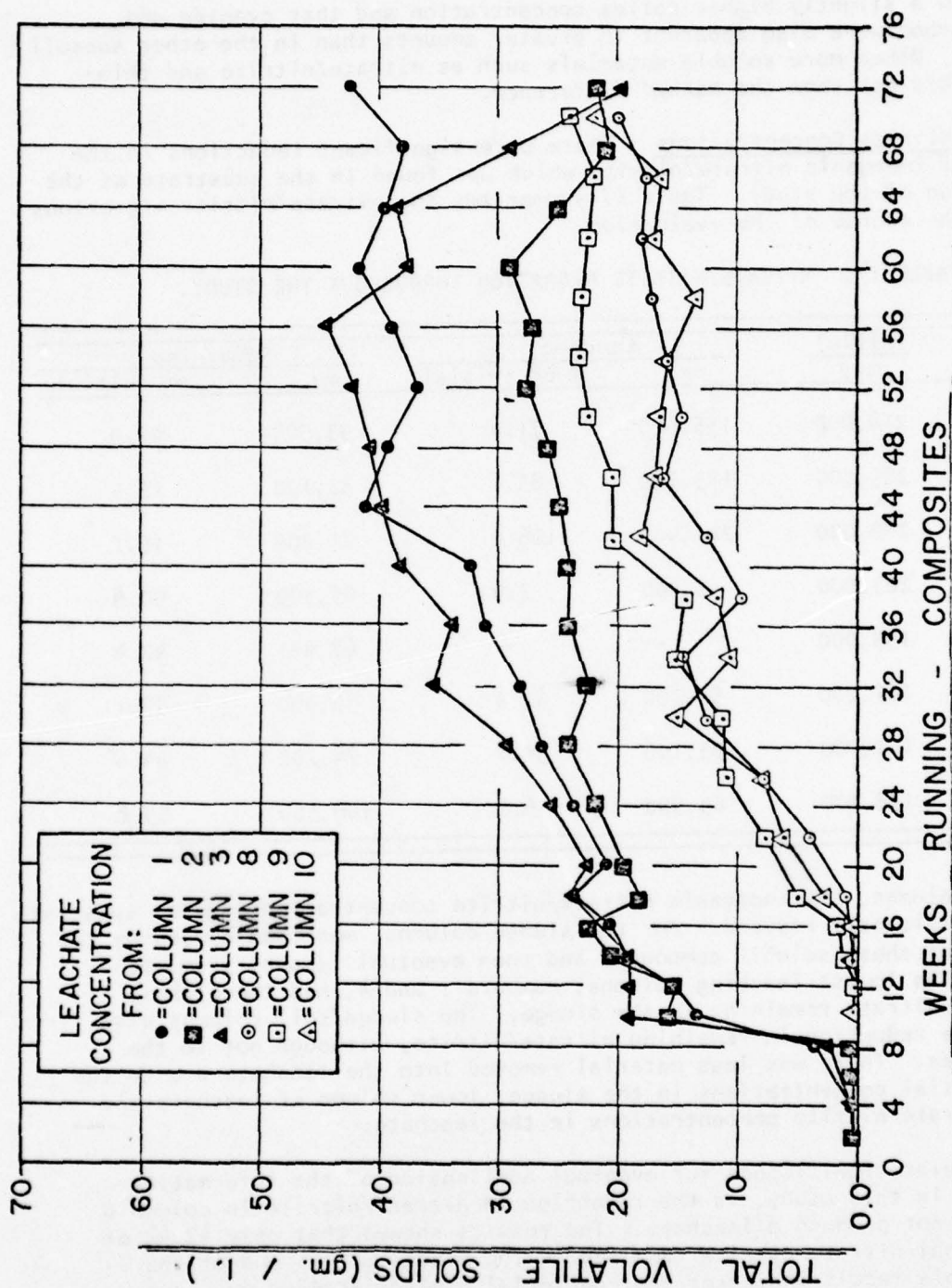


Figure 7. Variation of total volatile solids with time.

formation of a 2.5 - 5 cm (1-2 inch) hardened layer at the interface supported this belief. Analyses of this layer in columns 3 and 9 indicated that it contained a slightly higher solids concentration and that cyanide and total carbon were also apparent in greater amounts than in the other subsoil samples. Other more soluble materials such as nitrate/nitrite and thio-cyanate did not show the marked difference.

Nitrate/Nitrite Concentrations - There were significant reductions in the amount of inorganic nitrate/nitrite which was found in the substrate at the conclusion of the study. Table 17 summarizes the nitrate/nitrite migrations during the course of the evaluation.

TABLE 17. NITRATE/NITRITE MIGRATION THROUGHOUT THE STUDY.

Column number	Initial	Leached		Remaining	
	mg	mg	% of initial	mg	% of initial
1	218,000	155,600	71.4	93,500	42.9
2	209,000	173,700	83.1	32,100	15.4
3	209,000	221,400	106.0	21,200	10.1
4	203,000	5,900	2.9	103,300	50.9
6	159,000	--	--	67,431	42.4
8	167,000	54,100	32.4	95,400	57.1
9	167,000	93,100	55.7	74,200	44.4
10	178,000	65,500	36.8	106,500	59.8

For all columns, the inorganic nitrate/nitrite concentrations in the substrate were significantly reduced. For the sludge columns, most was caused by the leaching of these soluble compounds and then eventual removal from the system. The lowest leaching columns, numbers 1 and 4, had the highest amount of nitrate remaining in the sludge. The sludge/soil columns also showed the reduction in remaining nitrate/nitrite, although not to the same degree. There was less material removed into the leachate due to the lower initial concentrations in the sludge, lower volume of leachate and lower nitrate/nitrite concentrations in the leachate.

Of particular significance for eventual application of the information collected in this study, is the reduction in nitrate/nitrite in column 6 which did not produce a leachate. The results showed that only 42.4% of the original nitrate/nitrite remained in the sludge at the end of the study. This result indicates that bacterial denitrification may have occurred within the system which could account for the changes.

Organic Nitrate - The organic nitrate ester concentrations and absolute amounts in both the sludge and the sludge/soil declined significantly over the period of the study. No organic nitrate ester was leached, so the entire decline can be attributed to either chemical or biological degradation within the substrate. Table 18 presents the initial and final concentrations and amounts of organic nitrate in the various columns.

Overall, the sludge/soil columns had lower concentrations and amounts of organic nitrate remaining in the substrate. This is most likely due to a biological degradation process which could involve microorganism consumption of the NC degradation products. This would force the equilibrium to encourage chemical NC degradation. It is also possible that the NC is utilized directly by acclimated organisms. A comparison of the leaching columns (8, 9 and 10) to the column which did not leach (#6) shows that the NC degradation continued at a faster rate in the undisturbed column. This also could indicate the occurrence of a biological impact on the system.

Column #3, a sludge column dosed at the highest rate, also showed the extreme drop in organic nitrates which corresponded to the results of the sludge washing tests described earlier. Again, in the chemical degradation of NC, the equilibrium appears to be disturbed, although in this system it is probably due to the physical removal of the reaction products in the leachate. The sludge columns also exhibited a more pronounced variation in concentrations with depth. This could indicate that the frontal passage of leaching water and the associated volume differences impact the end result.

Total Organic Carbon - TOC was one of the most difficult parameters to measure in the NC limed sludge. Surprisingly, the concentrations of TOC in the substrate increased significantly during the study (see Table 19). This occurrence is difficult to explain. Possibly the errors associated with the analytical method influenced the results, however, this would be unlikely to cause such significant differences. It may be possible that some types of inorganic carbon are being fixed by autotrophic or other bacteria, however, this evaluation did not confirm the effect. Significant amounts of TOC were removed in the leachate, especially from the sludge columns. However, the concentrations of TOC in the final sludge samples still exceeded initial amounts.

Solids Concentrations - The solids concentration of the sludges and sludge/soil remained approximately the same throughout the study. There was a small increase in solids concentration with depth in most columns. Possibly this could be due to the natural drainage of the sludge immediately over the sandy subsoil.

Cyanide/Thiocyanate Concentrations - One of the most surprising results of the study was the high concentrations of total cyanide measured in the sludge and the sludge/soil. Table 20 presents the actual results obtained using the modified analytical technique described earlier. Figures 8 and 9 have been prepared which present the variation in cyanide concentration by column type and depth.

TABLE 18. ORGANIC NITRATE CONCENTRATIONS IN SLUDGE WITH DEPTH.

Parameter	Units	Sludge, #1	Sludge, #2	Column Type		Sludge, #4	Sludge/ soil		Sludge/ soil		Sludge/ soil	Sludge/ soil
				Sludge, #3	Type		#8	#9	#10	#6		
Initial org. nitrate	mg/kg dry	699	699	699		699	202	202	202	202		
Substrate, 15 in.	mg/kg dry	80	51	136		121	15	<16	50	<15		
Substrate, 25 in.	mg/kg dry	64	201	11		224	55	6	7	<16		
Substrate, 35 in.	mg/kg dry	277	121	36		82	<17	7	55	6		
Substrate, 44 in.	mg/kg dry	107	185	59		78	55	54	23	69		
Substrate, 65 in.	mg/kg dry	156	262	171		110	78	47	39	30		
Subsoil	mg/kg dry	<12	<12	12		13	47	<12	<11	<11		
Subsoil	mg/kg dry	<12	<12	<12		<13	<12	<12	<12	<12		
Initial amount	mg	6,467	6,169	6,162		5,976	4,500	4,505	4,783	4,221		
Final amount	mg	1,830	2,039	930		1,184	2,241	1,238	1,327	623		
Leachate volume	ml	15,886	20,187	24,239		783	8,894	12,358	10,054	0		

cm = inches x 2.54

TABLE 20. CONCENTRATION OF CYANIDE IN COLUMNS BY DEPTH.

Depth of sample, inches	Column number											
	1	2	3	4	5	6	7	8	9	10	11	12
15"	163*	149	160	414	<16	51	-	38	44	60	-	-
25"	361	251	247	434	-	86	48	59	80	-	<16	<16
35"	371	308	251	475	-	105	-	98	89	-	-	-
45"	520	343	253	523	-	200	-	138	102	-	-	-
55"	478	323	335	524	-	265	-	145	152	-	-	-
69"	<16	<16	<16	106	-	<16	-	10.8	<16	169	-	-
95"	<16	<16	16	121	-	<16	-	<16	18	-	-	-

*All concentrations in
mg/kg - dry weight
cm = inches x 2.54

TABLE 19. MIGRATION OF TOC THROUGH SYSTEMS.

Column number	Initial, mg TOC			TOC Analyses				Final, mg TOC		
	Sludge	Soils	Total	Sludge	Soil	Leachate	Total			
1	596,000	27,000	623,000	739,000	64,000	54,000	857,000			
2	568,000	27,300	595,300	737,000	65,000	58,000	860,000			
3	568,000	27,000	595,000	702,000	143,000	89,000	934,000			
4	555,000	27,000	582,000	640,000	79,000	1,600	720,600			
8	515,000	27,300	543,000	670,000	74,000	9,200	753,000			
9	515,000	27,500	542,500	542,500	480,000	24,000	568,000			
10	547,000	27,500	574,500	629,000	68,000	9,300	706,000			
6	493,000	27,200	520,000	530,000	96,000	--	626,000			

The cyanide concentrations were highest in the sludge columns probably because there was a greater initial amount of NC in these systems. Values range from approximately 200-500 mg/kg-N dry weight. The degradation of NC to cyanide does not appear to be caused or hastened by the rate of dosing since columns 4 and 6 which did not produce significant leachate contained large amounts of cyanide. The final amount of cyanide in the columns did appear to be affected by leaching since the overall concentrations in the leached columns were lower. This could be due to the removal of cyanide with the leachate or by hastened biological activity.

The cyanide measured in the sludge and sludge/soil are probably present as complex organo-cyanides since only low concentrations of cyanide migrated to the leachates. It is likely that the cyanides are complexed with particulates which are removed by the first layer of subsoil. This phenomenon is illustrated in Figure 8 since the cyanide concentrations corresponding to the greater depth subsoil were much lower than the others.

The concentrations of cyanide did increase with depth in the sludge or sludge/soil (see Figure 9). There appeared to be a frontal movement which involved a steady increase until the interface between the substrate and the subsoil. Figure 8 also shows the difference in cyanide concentrations in the sludge columns (1, 2, 3 and 4) and sludge/soil columns (6, 8, 9 and 10) which showed that sludge/soil leachate had lower cyanide concentrations than that produced by the sludge only columns.

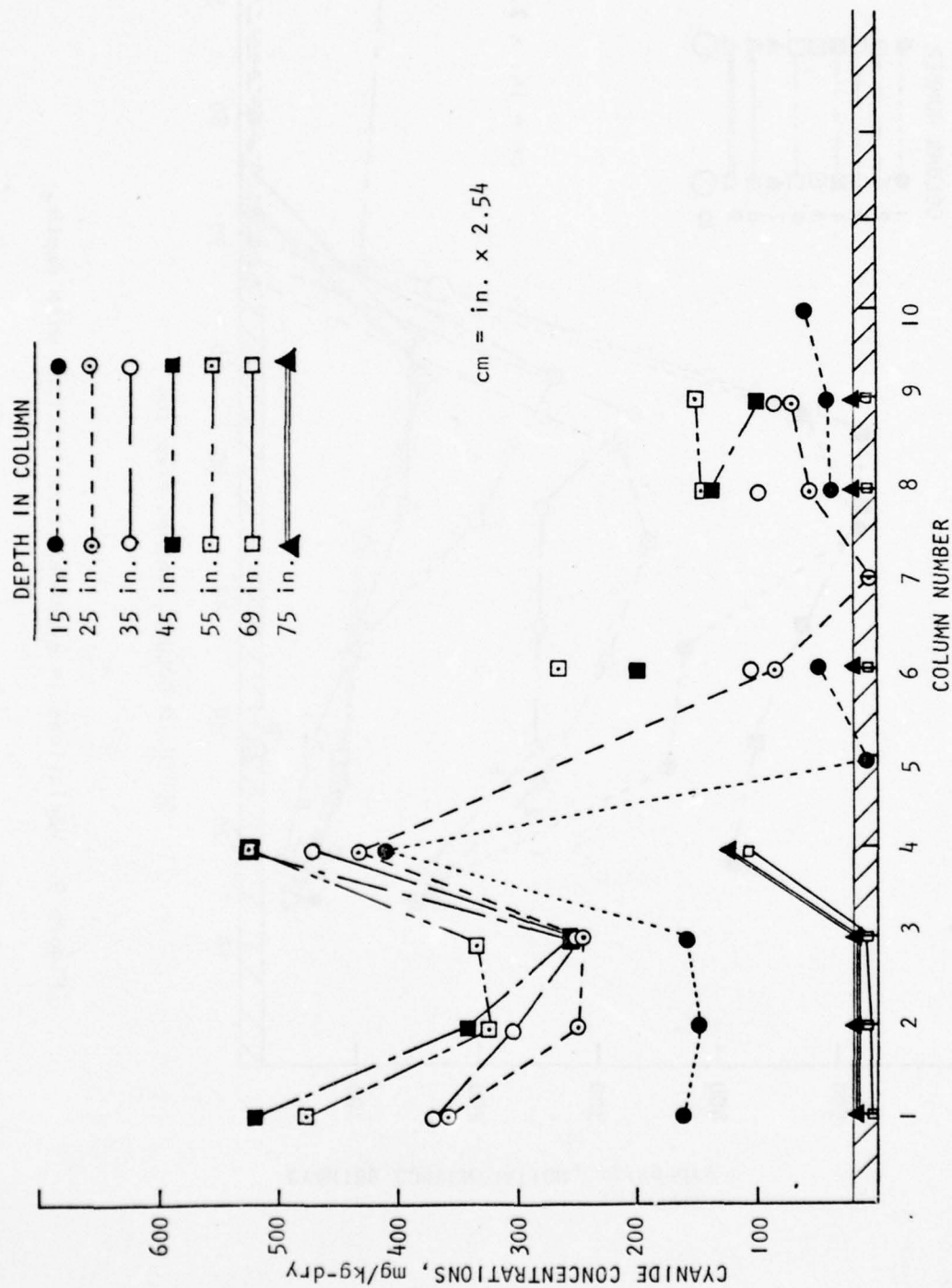


Figure 8. Variations in cyanide concentrations by column number.

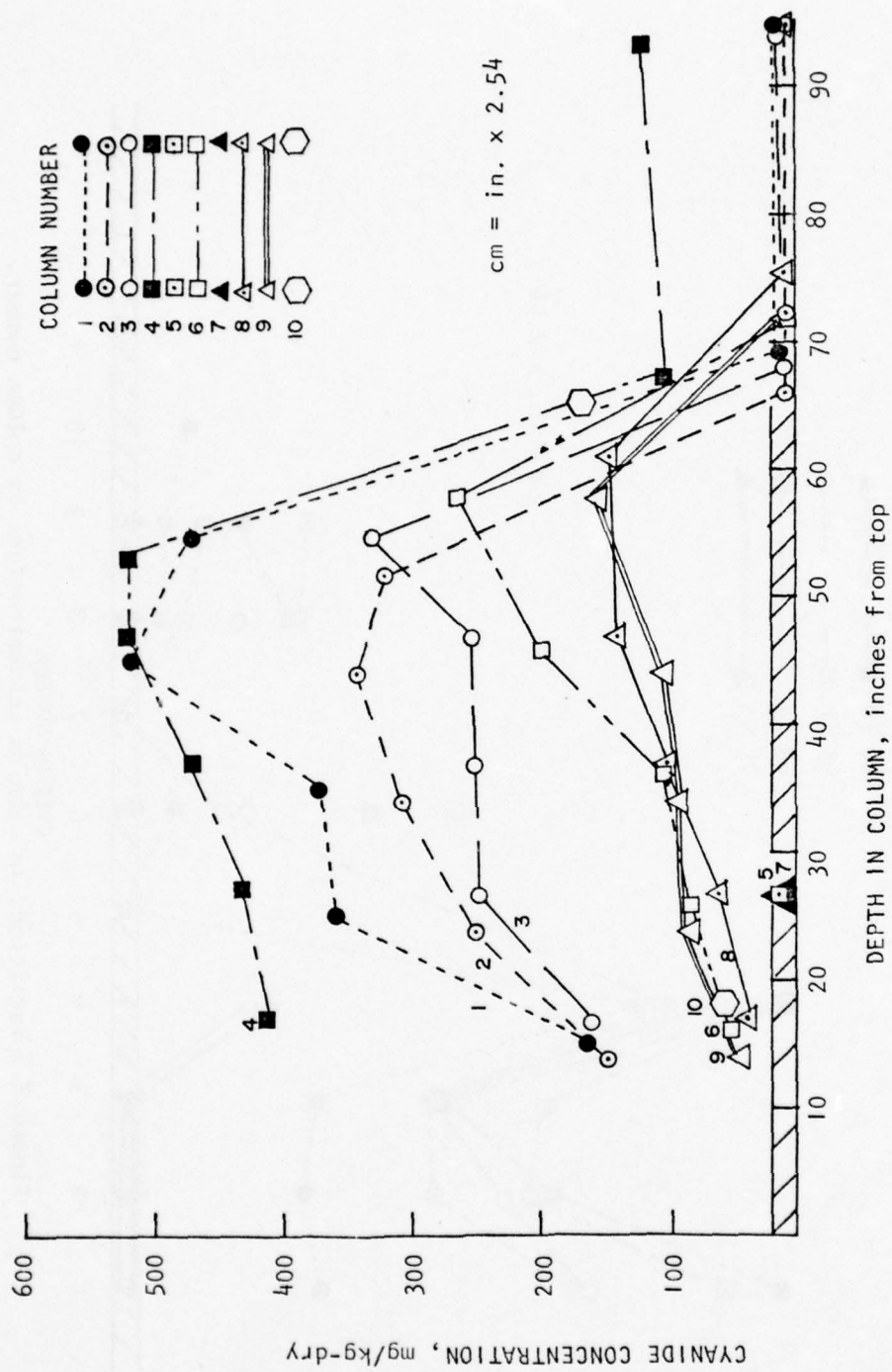


Figure 9. Variations in cyanide concentrations with depth.

Thiocyanate concentrations were much less significant in the substrates. These appeared to be more leachable since the sludge and sludge/soil concentrations were similar to those measured in the leachate samples.

System Evaluation

In order to trace the various nitrogen forms within the column system, mass balance calculations for nitrogen within the columns were performed. These involved summation of initial and final nitrogen contributed by TKN, ammonia, inorganic nitrate/nitrite and organic nitrate. The results in terms of percent recovered are summarized in Table 21.

TABLE 21. NITROGEN MASS BALANCE RESULTS.

Column number	Type	Percent recovered
1	Sludge	105
2	Sludge	91
3	Sludge	94
4	Sludge-inundated	50
8	Sludge/soil	79
9	Sludge/soil	87
10	Sludge/soil	84
6	Sludge/soil - inundated	37

Overall, the sludge/soil columns showed lower recoveries of the nitrogen forms than that in the sludge only columns. For both substrates, the inundated columns which were basically not leached showed markedly less nitrogen recoveries. The results with respect to sludge/soil recoveries again indicate the possible existence of denitrifying bacteria in the sludge/soil substrate. Although the study was not designed to allow positive identification of denitrifying organisms, their presence can be inferred from a number of factors. The conditions in the column were appropriate for denitrification since the system was anaerobic and a substantial organic substrate was available in the nitrocellulose and its degradation products. The only problem could be the high pH in the subsoil system. However, the soil does have a certain amount of buffering capacity which is shown by the neutral pH of the collected leachate. It is hypothesized that the soil could neutralize enough of the sludge alkalinity to allow a compatible environment for the bacteria.

To confirm the possible presence of bacteria, total coliform analyses were performed on leachate from sludge, sludge/soil and control columns. The sludge columns leachate contained no bacteria, while that from both the control and the sludge/soil columns had significant coliform contents. Although these results do not confirm the presence of denitrifying bacteria, it does indicate that the environment in the sludge/soil has been modified to the point where bacteria growth is possible.

LAND DISPOSAL ALTERNATIVES FOR NC LIME SLUDGES

General

It is not within the scope of this project to develop or design the actual land disposal operations for the NC-lime sludge which was under study. To do this properly requires sufficient first hand geological and hydrological information on the various sites being considered. Contact must be made with the appropriate state or federal regulatory agency to obtain the necessary permit and land disposal information and specifications. Finally, up to date data on sludge quantities, present day sludge characteristics, and anticipated future changes in sludge quantity and characteristics should also be known.

The results of the column studies on the NC-lime sludge presented in this report do provide some guidance and direction as to the land disposal of this material. In fact, one of the principal objectives of this study was to determine the characteristics and quantity of leachate generated from the columns containing various combinations of sludge and soil, so that this information can be used in the selection and operation of a landfill site. Very useful information as to the permeability of the material, its fate under "long-term" storage, and the characteristics of the leachate have been derived which will be a definite help in the site selection process. As an example, one of the important findings of the study program was that nitrocellulose fines did not leach out of the sludge in any of the test columns used. The significance of this finding alone in any subsequent landfill operation of the sludge is apparent.

The purpose of this section of the report is to present NC-lime sludge land disposal alternatives in light of the results from the 22 month column dosing program. Particular attention will be given to land disposal considerations that are applicable to hazardous type wastes because of the likelihood that the NC-lime sludge will be classified into this category.

Hazardous Waste Criteria

Since October of 1976, the US EPA has been involved in developing criteria for use in identifying hazardous waste as required by the Resource Conservation and Recovery Act (RCRA). Draft regulations have been prepared and circulated to various individuals and groups both within and outside the federal government. It is not the purpose here to decide whether the NC-lime sludge meets any of the proposed criteria for a hazardous waste, but rather to suggest the hazardous waste categories that the material might be classified under by those who would be responsible for making this decision. The possibility that the NC-lime sludge will be classified as a hazardous waste must be considered seriously prior to establishing any future land disposal practices. If the sludge is not eventually judged to be a hazardous waste, the less stringent land disposal practices of those discussed in this section would probably then apply. In this case the land disposal practices will be of the same type normally employed for "typical" municipal refuse.

Six different hazardous waste criteria have been advocated by the US EPA. These are: flammability, corrosiveness, infectious agents, reactivity, radioactivity and toxicity. The two criteria which might apply in the case of the NC-lime sludge are reactivity and toxicity. Among the properties cited for reactive wastes are wastes which in themselves are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures. The NC in the sludge may cause it to meet this criteria. Wastes can be considered toxic if the leachate from the particular waste has any constituents with a concentration ten times the concentration for the same constituent in drinking water. The high concentration of nitrate in the leachate from the NC-lime sludge which was consistently noted in this study could be the cause for classifying this material as a "toxic waste" and hence as a "hazardous waste" under RCRA. A final possibility exists with respect to the high cyanide concentrations in the sludge itself. Since cyanide is also controlled by drinking water regulations and is a priority pollutant, this parameter could also result in the classification of the NC-lime sludge as a hazardous waste.

General Approaches in the Land Disposal of Wastes

There are basically two different approaches which can be employed in the land disposal of solid wastes. The first is to deposit the wastes on the land with the primary objective that the material will remain unaltered or degrade very slowly, such that the impact of the wastes on the surrounding soil environment is minimal. This has been referred to as the "high and dry" or "containment" approach. The second is almost the opposite of the first, when an attempt is made to maximize the rate of degradation or stabilization of the deposited waste by placing the material on an impervious bottom, passing water or recirculated leachate through it at an "optimal" rate, and using a leachate collection system for subsequent leachate management, either on or off the site. This has been referred to as the "controlled high rate stabilization" approach.

Containment - One of the principal requirements in the containment approach is the selection of a landfill site with suitable geological and hydrological properties. Every effort must be made to keep the amount of water entering the deposited waste to a minimal level. This includes water which originates from both precipitation, part of which percolates through the deposited waste, and ground water in the zone of saturations which can move upward or laterally, depending on the hydrogeology of the site.

The amount of water which reaches the wastes from precipitation can be kept to a minimum by selecting a site of low soil permeability. This soil characteristic is generally provided by unconsolidated formations consisting of varying proportions of clay, silt, fine sand and loam. Conversely, unconsolidated materials of coarse sand and gravels with high permeabilities, or consolidated materials such as limestone or shale with fissures, faults or fractures of any kind, will not prevent water from reaching the deposited wastes, nor prevent the leachate from rapidly emanating from the site, which from the standpoint of containment, is very undesirable. While each site must be considered individually, soil permeabilities in the range

of 10^{-6} to 10^{-8} cm/sec are normally required to achieve a suitable containment environment for the wastes.

The main reason for the low permeability soil requirement is to provide sufficient time for the attenuation of any leachate which originates from the wastes. Attenuation refers to the combination of rather complex physical, chemical and biological forces which bring about an improvement in the leachate quality as it passes through the soil. Soil microorganisms, adsorption, ion exchange, precipitation, straining and dilution are all involved to varying degrees in the leachate attenuation process. A low permeability soil assures that a limited quantity of leachate will be produced and that because of the low ground water movement velocities, sufficient time will be provided for the various attenuation mechanisms noted above. Obviously, containment of the deposited wastes under such conditions will keep the material in a virtually unchanged state for many decades.

Another requirement which must be met to achieve waste containment is that sufficient distance be provided at the site between the lowest point in the deposited wastes and the highest elevation of the ground water table. This distance depends on the soil permeability at the site, but many investigations have suggested a minimum distance of 3m (10 ft). Greater distances are desirable, especially in high precipitation areas and in situations where infiltration conditions tend to be on the higher side. Again, the greater this distance, the greater will be the time for attenuation mechanisms to take place, and the less will be the adverse impact on the surrounding ground water body.

Proper waste containment also requires that surface runoff be controlled within and around the landfill site, and that suitable waste placement practices be employed. Surface runoff can be managed through proper site planning, through the use of slopes, channels, embankments, suitable cover soil and other sound hydrological practices. Surface water should not be allowed to pool on the site, especially in the region where the wastes are being deposited, since this will enhance the leachate production potential. Care should also be exercised in sloping or "mounding" the deposited wastes so that any water which infiltrates the cover soil does not pool above the material, but rather tends to move laterally. Also, daily and final cover material should have characteristics for good compaction to minimize infiltration of precipitation. Quick seeding of the cover soil with a suitable form of vegetation will promote evapotranspiration, and hence limit the amount of water which reaches the deposited wastes.

Apart from the normal landfill covering practices noted above, it is possible to engineer a cover of very low permeability, or of even total impermeability, if desired. This can be done by the proper selection of characteristics, thickness and compaction of various clays designed for this purpose. Often times such clays are not available at the site and must be imported. To achieve total impermeability it is possible to use a plastic or asphaltic liner between the deposited waste and the soil cover,

with precautions taken to assure that no pooling of infiltrated water occurs. A major concern with impermeable covers is that provisions must be made for gas release or management if the nature of the waste is such that gas formation (e.g., carbon dioxide, methane, nitrogen, etc) is possible. Obviously, the containment approach is greatly enhanced in landfill designs where impermeable covers are employed, and ground water table distances are 15 meters (50 ft) or more below the bottom of the deposited wastes.

Controlled High Rate Stabilization - The primary objective with the use of this approach is to provide the most suitable environment in the deposited wastes for degradation or stabilization of the waste constituents. This is generally accomplished by passing sufficient quantities of infiltrated precipitation or recirculated leachate through the waste mass. The process is continued until the wastes are "stabilized", that is, the leachate constituents are of low enough concentration such that the impact on the ground water in the vicinity of the landfill site is minimal. The length of time required to stabilize the waste depends on the nature of the deposited material, depth of the cells, rate of water or leachate percolation through the wastes, and other factors such as pH, temperature, nutrients, toxic materials, etc. Unfortunately, there is very little full scale operating experience with this type of system to estimate such duration periods, even with municipal refuse, much less with various types of industrial and special wastes.

The use of this type of an approach requires the installation of an impermeable bottom liner and a leachate collection system. Impermeable liners can be constructed of asphalt, various types of plastics, butyl rubber, compacted clay, and mixtures of native soil with such materials as montmorillonite, bentonite, cement, lime and fly ash. Consideration must be given to the nature of the wastes so that the liner design is compatible with the deposited material. It is essential that there is no passage of leachate through the liner.

Leachate collection systems generally consist of perforated plastic pipe or spaced cement or clay tile laid on the liner and generally sloped to central collection points, such as manholes. The tile is generally covered with a suitable layer of graded gravel and coarse sand. Sufficient water is allowed to infiltrate the deposited wastes to produce a leachate. During dry periods all or part of the leachate can be recirculated through the wastes. The excess leachate must be treated with either an on-site facility or directed to a sewer system for treatment in a municipal treatment plant. One must keep in mind that this approach also produces a residue or sludge which must eventually be "disposed" of properly.

Combined System - It is possible in some situations to use a combined containment/stabilization approach in the land disposal of wastes. In these cases, the design and operation of the site is approached from the standpoint of containment, with the added feature of a leachate collection system installed at the bottom of the waste cells. The native low permeability soil of the site serves as a modified bottom liner. If designed properly, little or no leachate should be collected. In the event that some accumulates, it would normally be pumped out and transported

from the site to a suitable treatment location.

Special Considerations for Hazardous Wastes

Draft regulations have been prepared pursuant to the requirements of RCRA on the storage, treatment and disposal of hazardous wastes. While it is not the intent to present the detailed draft regulations in this report, since they are too voluminous and subject to considerable change in the initial formative years, a brief discussion of some of the salient points will indicate the general trends and expectations in this area.

The draft regulations call for a ground water and leachate monitoring system at all landfill sites for hazardous wastes, including vacuum lysimeters in the zone of aeration to detect leachate. Both upgradient and down gradient monitoring wells will have to be provided in the zone of saturation. Sampling frequencies and analysis requirements will be specified for the various types of samples collected.

The draft regulations provide for the use of either a natural containment system or a system that provides for leachate collection. The main requirement in either case is that there not be a direct hydraulic connection between the disposal site and surface or ground water. Minimum distances are specified from bottom of landfill to high ground water levels and from site to private water wells. Site locations within major drainage areas are discouraged. Natural containment landfills will have to be located in areas where it is possible to provide a natural soil liner under the landfill which is at least 3m (10 ft) thick and has a permeability of less than 10^{-8} cm/sec. Leachate collection systems will have to be constructed on bottom liners of natural soils at least 0.61m (2 ft) thick with permeabilities of less than 10^{-7} cm/sec. These soils must be compatible with the waste to be landfilled. The draft regulations also include specifications for hazardous wastes treatment facilities which would have to be considered since the leachate collected from a hazardous waste landfill site will have to be treated as a hazardous waste.

Finally, the draft regulations also consider such landfill operating requirements as training of operators, recordkeeping and reporting, contingency plans, financial responsibilities, and closure and long term care provisions among others. Final soil cover specifications will be given for various closure arrangements. The draft regulations state that, "soil cover integrity, slopes, vegetation cover, diversion and drainage structures, and ground water monitoring facilities shall be maintained for the time period that the hazardous waste may pose a threat to the environment".

Land Disposal of NC-Lime Sludge

While, as noted previously, it is not the intent here, nor is it possible, to design the NC-lime sludge disposal facility, the results of the column study do suggest possible approaches and directions which should be considered. One of the initial concerns was whether or not NC fines leach

out of the sludge during the dosing operation. The results of 22 months of dosing demonstrated clearly that this does not occur. One would not expect to find these fines in a leachate from a full scale landfill operation, if a leachate is in fact generated. If a natural containment approach is employed, a small quantity of fines, if generated, would most probably be effectively removed in the top few inches of a low permeability soil beneath the deposited sludge. This phenomenon was illustrated in the column study by the hardened interface layer between the substrate and subsoil.

A characteristic of the sludge which is particularly important in a future land disposal scheme is the extremely low permeability exhibited in the columns. The mixture of sludge/soil had even lower permeabilities in the system. These indications are encouraging, however, the actual permeability tests performed by a soil testing laboratory indicated that the systems exhibit a tendency to channel under higher pressures (see Appendix for detailed report of the results). Therefore, the effective permeability would be much greater and the use of the sludge or the sludge/soil mixture as a liner may not be acceptable. It may be possible to mix a ratio of sludge and soil which does exhibit consistently low permeability. Available fly ash wastes could also be incorporated. These types of tests have not been performed. If an impermeable mixture can be found, it may be feasible to utilize the natural containment landfill approach if the disposal site has suitable geological and hydrogeological characteristics. After mixing the sludge with a suitable amount of soil, the mixture could be deposited in properly mounded cells, so that any water which infiltrates through the final cover will not tend to pool on the cell surface. Although a well composited, low permeability fine cover soil would normally be required, its permeability may not be as low as the permeability of the sludge/soil mixture. This should not cause a problem if the waste cell surface slopes away from a central high point.

Very high nitrate/nitrite concentrations were obtained in the leachate from all of the sludge containing columns. The column dosing rates were 2.54, 5.1, 7.6cm (1, 2 and 3 in.) per month. It is apparent that if large quantities of water are allowed to percolate through the deposited sludge, very high nitrate/nitrite concentrations will be present in the leachate. Because of the high solubility of these ions, they will pass unimpeded to the ground water body. It is also apparent from the results of the column study, that this leaching process will continue for some time due to high nitrate/nitrite concentration in the initial or "fresh" sludge. This high concentration is first elutriated by the percolating water with the long term degradation of the nitrocellulose fines also serving as a source of these ions. The use of a natural containment land disposal approach would appear to be a reasonable means of managing the high nitrate/nitrite concentrations in the leachate. Limiting the amount of water which can enter the deposited sludge will result in a small amount of leachate generated.

This containment technique may be even more desirable when landfilling a mixture of sludge/soil. The study results indicate that bacterial denitrification probably occurred in the sludge/soil systems although it

was not as extensive in the sludge only columns. Containment of the sludge/soil mixture could allow the denitrification to occur which may reduce the potential nitrate concentrations in any leachate which may result. Also, the biological activity can continue over an extended period of time and decontaminate much of the sludge mixture. Any leachate which would be generated is expected to be so low in volume that the dilution with groundwater may be a major attenuation mechanism.

Consideration should also be given to the velocity of the ground water body and the distance between the disposal site and the nearest drinking water well in the final site selection process.

The containment approach for the land disposal of the sludge or a sludge/soil mixture would also appear reasonable for the management of the high TOC concentrations which occurred in the column leachates for the same reasons cited in the case of the nitrate/nitrite values. The TOC associated with the sludge/soil mixtures could also be reduced by denitrification in a containment system. Further attenuation by microorganisms presents in the subsoil is also anticipated. Therefore, the buildup of TOC in the ground water in the vicinity of the landfill site is very unlikely.

Cyanide migration could also be minimized if a containment technique is used for disposal. The subsoil filters most of the complexed cyanides from the leachate, however, potential soluble cyanide concentrations remain objectionable. Reduction or elimination of leachate by containment is a beneficial approach to handling the problem. In addition, biological degradation could occur in the sludge/soil system which reduces concentrations of cyanide in the substrate, as well as the leachate.

As expected, the concentrations of COD, total solids, total dissolved solids, total volatile solids, dissolved volatile solids and conductivity were also quite high. Limiting the amount of water which can infiltrate the deposited sludge should release these constituents at a low enough rate to allow attenuation by microorganisms so that the ground water quality in the vicinity of the landfill site is not adversely affected. Again, dilution provided by the ground water body may be a principal attenuation mechanism in the case of the inorganic constituents, whereas it will be biochemical degradation and dilution in the case of the organic constituents. The organic nitrogen, alkalinity and pH values of the leachate should not cause any problem in a full scale operation.

It should be kept in mind that the whole idea behind the containment approach is to keep the deposited sludge as dry as possible so that a minimal amount of leachate will pass into the soil beneath the deposited sludge. This means that the deposited sludge will remain virtually unaltered in the ground for many years, and that the "stabilization" of the sludge will continue for generations.

General References on Land Disposal of Sludge

It is not within the scope of this report to present an extensive literature review on the subject of sanitary landfills. Because of the unique

characteristics of the NC-lime sludge, much of this literature would be of limited usefulness. There are some literature sources, however, that can provide some useful background information on landfilling of wastes in general, geological and hydrogeological considerations, hazardous waste management, and the use of landfill liners and covers. These literature sources are included as an aid to those who must use the results of the column study represented in this report, as an aid in the eventual design and operation of a full scale NC-lime land disposal operation. Needless to say, such individuals would have to be aware of the latest State of Virginia and US EPA regulations on landfills, as well, particularly if the wastes are categorized as hazardous.

There have been a number of reports and papers published within recent years on the design and operation of sanitary landfills, and on the environmental concerns associated with the leachate and gases generated therefrom. Though most of these sources are primarily concerned with municipal refuse, much of the information is applicable to the land disposal of wastes of any type. In addition, some of the sources include separate sections on special problems related to the handling and disposal of hazardous and toxic wastes. The most useful of these sources published in the last half dozen years were written by Brunner and Keller (6), American Society of Civil Engineers Solid Waste Management Committee (23), Pohland and Engelbrecht (24), Zanoni (25), Reindl (26), Thompson and Zandi (27), and Caffrey, David and Ham (28). Fields and Lindsey (29) of the US EPA wrote a short, useful report on the land disposal of hazardous wastes.

Hughes, Cartwright, Griffin and other with the Illinois State Geological Survey have written a series of very informational reports on geological and hydrogeological considerations in the selection and operation solid waste disposal sites (30)(31)(32)(33)(34)(35). Although most of the data were obtained from full scale landfill sites in Northeastern Illinois, many of the principles and conclusions derived from their work would be applicable to other sites as well. Among other things, included in the reports is useful hydrogeologic and geologic criteria for the site selection process, information on leachate production and attenuation in the soil regime, the use of landfill covers and bottom liners, some discussion of leachate collection and treatment systems, monitoring ground water in the vicinity of landfill sites, the effectiveness of various types of clays in the attenuation of various leachate constituents, and examples of different landfill designs for varying site geologic and hydrogeologic features. Schneider (36) of the US Geological Survey wrote a short general paper covering hydrologic considerations in the site selection process.

Very little has been written to date on the use of liners and special covers for land disposal sites. Probably the most comprehensive report was written by Geswein (37) of the US EPA, covering such topics as type of materials, construction methods, costs, etc. Short overview papers on this subject have also been written by Dallaire (38) and Kumar and Jedlicks (39).

SUMMARY

When the final results of the study are evaluated, certain aspects appear to be most crucial and have significant bearing on determination of the feasibility of landfill disposal for NC limed sludge. These findings and their impacts have been discussed in detail in the previous parts of this section and, for convenience, they are summarized in the following paragraphs.

Sludge Quality and Quantity

The results of the sludge analyses indicated that according to proposed regulations under RCRA there is a high likelihood that the NC lime sludge will be classified as a hazardous waste. This categorization can be the result of at least three characteristics. The first is the NC content of the sludge which could cause the material to be considered reactive. The second is the extremely high concentrations of inorganic nitrate/nitrite in the sludge. These result from the initial NC processing steps (nitration in a mixed acid bath) plus some chemical additions which can contain nitrate. Removal of the high nitrates by washing is possible but may be difficult to implement because of the high volumes of wastewater required and the problems in treating a nitrate waste. The cyanide concentrations in the sludge may also contribute to the NC lime sludge being classified as hazardous. Although no cyanide is used in the manufacturing process, significant amounts of cyanide are generated by the degradation of the NC. There may not be much cyanide present initially, but the compound does appear to accumulate over time.

The amount of sludge generated is difficult to establish. Modifications to the system have limited the major source of NC fines at this time to the alcohol rectification system. The volume of sludge generated will be a function of manufacturing rate, dewatering techniques and eventual process changes.

Leachate Quality and Quantity

One of the most significant findings was that the nitrocellulose fines did not migrate with the leachate. Throughout the course of the study, all nitrocellulose concentrations in the leachate were below detection limits (1-10 mg/l). However, the soluble contaminants were readily removed from the sludge or sludge/soil by the leaching rainwater. Most notable was inorganic nitrate/nitrite which was present in the leachate in concentrations up to 13,000 mg/l. Much of the leached nitrate was already present in the sludge when the substrate was placed in the columns. However, some was contributed by the continued degradation of the nitrocellulose in the alkaline environment. The trend associated with nitrate concentrations in the leachate was a flushing mechanism which resulted in a rapid increase in concentration up to a maximum level over a period of time followed by a more gradual concentration decrease.

The total organic carbon present in the leachate followed the same pattern of rapid increase, a maximum concentration, then a gradual decrease. The constituents of the organic fraction are most likely a variety of short

and long chain organic acids and other organic compounds.

Cyanide was a leachate constituent which was not initially anticipated. It was present in concentrations ranging from 1-20 mg/l. The sludge/soil columns contributed less cyanide to the leachate but values still ranged around 10 mg/l.

Leachate volumes were much lower than anticipated. The total volumes collected over the study period ranged from 19-23.5 l. When converted to bed volumes per month the sludge/soil columns leached 0.021-0.029 and the sludge columns produced 0.038-0.061. These small volumes of leachate were produced in a system designed to force leaching. Modification of the operation to minimize leachate production could eliminate all liquid produced.

Other Factors Impacting the Evaluation

There were several results noted during the study which have a significant impact on the feasibility of landfill disposal. One of the most significant results was the low permeability of the sludge and sludge/soil in the columns. This caused a low bed volume of leachate to be produced and should affect leachate volumes in a full scale system. However, the substrates may not remain impervious indefinitely under higher pressure. Special permeability tests were performed which indicated that the sludge and sludge/soil could channel when tested for permeability. This finding may limit the possibility of using the tested sludge or sludge/soil mixture as a lining material.

Another significant finding was that chemical degradation occurs in the sludge system and that biological degradation appeared to occur in the sludge/soil mixture. The chemical degradation of the NC was enhanced by leachate passage although it occurred in all systems. The biological degradation appeared to involve denitrification in the sludge/soil systems. The addition of soil seemed to buffer the environment to the extent that microorganisms could exist and the anaerobic conditions encouraged denitrification. This resulted in a less contaminated residual sludge and leachate. Both nitrate and TOC concentrations were significantly lower in the sludge/soil leachate and the substrate NC amounts in the sludge/soil substrate were also significantly reduced.

Finally, the subsoil provided a filtration media which trapped particulates and segregated them from the collected leachate. This was particularly noticeable for the cyanide compounds which were mostly concentrated in the substrate layer just above the interface with the subsoil.

Recommended System for Disposal

Landfill disposal of NC limed sludge does appear to be viable if proper precautions are taken and a containment approach is employed. Since the NC sludge will probably be considered hazardous, a liner and leachate collection system may be required along with various ancillary monitoring

wells. The leachate production should be minimized by the mounding of the NC sludge and covering of the area with a relatively impermeable cap.

In order to reduce the eventual hazard and to lower contaminant concentrations in leachates, the sludge should be mixed with soil prior to landfill. The exact amount of soil is unknown and should be evaluated so that the optimum condition can be achieved. This situation will allow the system to continue to biologically degrade throughout the life of the landfill. The more objectionable pollutants and contaminants including nitrates, cyanides, nitrocellulose and organic carbon should then eventually be converted into less hazardous materials including nitrogen, carbon dioxide and water. This will reduce the long term hazards associated with the landfill and should be beneficial to the overall operation of the waste treatment system.

SECTION VII

SULFIDE REMOVAL STUDIES

INTRODUCTION

The nitroglycerin waste stream from Radford included high concentrations of excess sulfide. It was anticipated that the oxygen demand exerted by the sulfide would have a detrimental effect on a proposed activated sludge process to which the waste stream was directed. The recommended sulfide concentration in wastewater influent is 1-10 mg/l to insure that the effluent from the plant contains less than the recommended maximum of 0.1 mg/l of dissolved hydrogen sulfide (40). In addition, high concentrations of sulfides are toxic to microorganisms in treatment plants. In the presence of non-acclimated sludge, sulfide inhibits biological growth at concentrations in excess of 25 mg/l (41). Therefore, oxidation of the sulfide was necessary prior to biological treatment of the nitroglycerin wastewater.

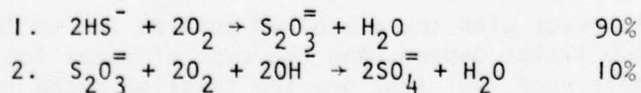
In order to determine which method of oxidation was most cost-effective, laboratory scale tests were conducted on samples of the nitroglycerin waste-stream. The results of the laboratory tests, the economic evaluation of the data and the recommended method for sulfide removal are presented in this section of the report.

TECHNIQUES FOR SULFIDE REMOVAL

There are several different methods which can be used to oxidize the sulfide to less harmful forms. These include chemical oxidation, precipitation, biological reactions, and ion exchange. Each of the methods has both advantages and disadvantages and these are briefly outlined in the following paragraphs.

Oxidation with Oxygen

The general reaction mechanism of oxygen oxidation (either air or pure oxygen) of sulfide is a two step process (42). The mechanism converts 90% of the sulfide to thiosulfate and 10% to sulfate.



The weight ratio of reactants for reaction 1 is approximately 1:1 oxygen to sulfide and 2:1 oxygen to sulfide for reaction 2. However, the oxidation alone will not completely remove sulfides since the rate of reaction

is a function of concentration, and since the equilibrium allows a residual amount of sulfide to remain in the wastewater. Oxidation of a water containing 270-1200 mg/l of sulfide may require 5-20 days to reduce the concentration to 1 mg/l $S^{=}$ (43).

Chlorination

Chlorine or hypochlorite solution can be used to oxidize the sulfide to various endproducts. The endproducts achieved are dependent mainly upon the chlorine dosage (44). The two general reactions are as follows:

1. $H_2S + Cl_2 \rightarrow 2 HCl + S^0$
2. $H_2S + 4Cl_2 + 4H_2O \rightarrow H_2SO_4 + 8HCl$

In reaction (1), where chlorine is added slowly with vigorous mixing, 2.1 ppm Cl_2 are required to remove 1 part of H_2S , however, the elemental sulfur which is formed must be removed by coagulation and sedimentation. If the chlorine dosage is increased to 8.4 ppm per ppm H_2S , the reaction will go directly to soluble sulfate endproducts. Nagano (45) studied sulfide oxidation and concluded that for sewage oxidation the reaction to form sulfates was predominant. However, it was also pH dependent, requiring additional chlorine at higher pH values. The reaction has been found to be extremely effective and can reduce concentrations of sulfides to zero.

Anion Exchange

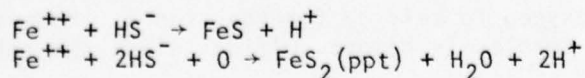
Ion exchange can be used to remove sulfide ions in certain situations (44). In general, basic ion exchange resins, regenerated with sodium chloride and/or sodium bicarbonate can be used to reduce the sulfide concentrations using the following mechanism:



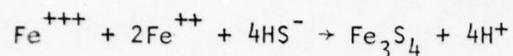
This technique, however, will result in a more concentrated backwash solution which will require further disposal. Anion exchange is also limited to waters with very low hardness and no iron concentration. In addition, the resins have low capacity and can only handle low flow rates (44). It is felt that this solution is not applicable since the NC wastewater contained high calcium concentrations (i.e., hardness) and some iron.

Metal Precipitation

Many metal salts will react with the dissolved sulfide ion to form insoluble sulfides. The insolubilities depend upon the type of metal ion used. Iron salts are commonly used (44) (46) and the reaction mechanism is as follows (47).



If a mixture of ferrous and ferric iron is added, the reaction is:



Therefore, the optimum mixture of ferrous iron to ferric is 1:2. Often oxygen is added to promote the precipitation of the iron sulfides, however, the oxygen catalyzes the reaction of iron sulfide to pure sulfur. As the reaction to sulfur is completed, some sulfide is returned to solution and therefore the effectiveness of iron for sulfide removal is reduced. Other metals can be used to precipitate sulfide in forms much more insoluble than iron. Examples of these materials are zinc, lead, mercury and silver.

Nitrate Reduction

The use of certain bacteria can remove the oxygen from the nitrate radical and create elemental N_2 . The nitrate reducing bacteria can then use the oxygen to oxidize sulfide if other oxygen is not available in the system. It is estimated that at least 10 times as much sodium nitrate is needed to oxidize a single amount of sulfide (48).

Hydrogen Peroxide

Hydrogen peroxide reacts with hydrogen sulfide to produce water and elemental sulfur (48). The theoretical reaction ratio is 1.1 H_2O_2 to H_2S but higher ratios are used in practice. This chemical has been used to reduce the amount of H_2S in sewers. However, in this application it is undesirable to form sulfur since then an additional coagulation and sedimentation step is needed.

Ozonation

Ozone has been tested to determine its effectiveness in oxidizing the sulfur. However, Pomeroy (47) found that ozone was no more effective in removing sulfide than pure oxygen due to the difficulty of injecting the gas into the water and the strong reducing power of sulfide. This factor indicates that further testing of ozone is unnecessary.

Other Chemical Addition

Other chemicals have been used to oxidize the sulfide. These are chlorate, chromate and permanganate. The chromium is effective but care must be taken to insure its discharge in the trivalent form since it too is toxic in very low concentrations.

Biological Treatment

Certain sulfur reducing bacteria can be used to reduce sulfide concentrations. A recent study on fellmongery effluent containing about 100 mg/l sulfides determined that red sulfur bacteria can reduce sulfide concentrations.

The reduction occurred in a lagoon with a detention time of 100 days at a temperature of 10-30°C (49).

Strippers

Stripping the H_2S gas in a controlled atmosphere is a common industrial technique for removals of high concentrations of sulfides. However, the waste gases from this process must be incinerated or recovered as sulfuric acid or sulfur. There are three common procedures used in stripping (50):

1. Stream or flue gas stripping.
2. Air oxidation to convert to thiosulfates.
3. Vaporization/incineration.

These procedures are quite efficient and remove 85-99% of the sulfides when acid addition for pH control to pH 4.0-5.0 (44) is used. The air oxidation as mentioned previously, combines the chemical oxidation with stripping to remove sulfides. However, all stripping processes require special handling on entrained H_2S . Unless a large volume of wastewater with high concentrations of sulfide is involved, a stripping column is not an economical approach.

For the application to the Radford nitroglycerin waste stream, it was desirable to utilize an oxidation technique which had relatively low detention times and formed soluble endproducts. In addition, since the flow rate was not great and the sulfide concentration was approximately 100 mg/l, use of expensive and complex processes was not practical. Therefore, the types of sulfide oxidation reactions to be studied were limited to aeration, oxygenation, chlorination, and UV light catalysis.

LABORATORY STUDIES

General

The laboratory study was divided into three separate tasks. The first involved collection and characterization of a nitroglycerin waste stream sample; the second involved preliminary tests of possible methods for lowering the sulfide concentration; and the third included the actual rate tests for the most feasible methods of oxidation. The results of these tests were used as a basis for economic evaluation of the various methods of sulfide oxidation.

Sample Collection and Characterization

It was necessary to test an actual sample of the high sulfide nitroglycerin waste stream, if possible. Therefore, 76 liters (20 gallons) of actual wastewater was shipped to the ESD laboratory for characterization and testing. However, when the sample arrived, it contained less than 1 mg/l of sulfide and was at neutral pH. It was hypothesized that the sulfide had been volatilized and lost during transport. Contact with the

Radford Arsenal officials (51) was made and it was determined that the sample should be spiked with approximately 100 mg/l sulfide as S^{2-} . The sulfide would be added in the form of $Na_2S \cdot 9H_2O$ until a 100 mg/l residual sulfide was measured. This procedure was to be utilized in all subsequent testing.

Since spiking could significantly alter some of the wastewater parameters, initial characterization of the wastewater was performed both before and after the sample was spiked. The results of these analyses appear in Table 22. A significant change involved the pH, however, in order to keep the sulfide in solution at a constant value, the higher pH was needed. Since uncontrolled evolution of H_2S is not an acceptable treatment technique, and since the wastewater stream is at a high pH through most of the unit processes, it was determined that maintaining the high pH was acceptable. Another consideration was that the amount of sulfide needed to reach a residual concentration of 100 mg/l was much greater than that calculated stoichiometrically. The stoichiometric value of 740 mg/l did not produce a residual of 100 mg/l and was increased to 1420 mg/l $Na_2S \cdot 9H_2O$ to reach the required amount. Therefore, some oxidation of sulfide may occur naturally within the wastewater, however, the amount cannot be accurately quantified due to changes in the sample from the initial sulfide loss and the spiking. If this is the situation, then the additional oxidant costs will be reduced during operation. One other observation was made when the sample was spiked with sulfide. Immediately after addition, the wastewater sample turned a turbid gray yellow and was further treated in this condition.

Preliminary Testing

Prior to performing actual rate tests, preliminary tests using oxidation techniques were done. Among the methods tested included oxygenation, aeration, chlorination, and UV light catalysis.

Chlorination Testing

The use of hypochlorite solution as the oxidant was tested first. It was desirable to force the reaction to form soluble thiosulfate and sulfate endproducts rather than elemental sulfur; so excess chlorine dosages were needed. The following free chlorine dosages were tested:

2222 mg/l
443 mg/l
665 mg/l
886 mg/l
1108 mg/l
1330 mg/l
1773 mg/l

The testing procedure used is outlined as follows:

Step 1: Place 500 mls of sample in a 1000 ml beaker.

TABLE 22. INITIAL ANALYSES OF WASTEWATER.

Before and After Spiking

Parameter	Units	Sample as received	Sample after spiking
pH	-	7.2	11.2
Nitrate	mg/l	8000	8500
Nitrite	mg/l	144	108
Chloride	mg/l	22	22
Alkalinity	mg/l	86	499
Sulfate	mg/l	900	940
Sodium	mg/l	1475	1610
TIC	mg/l	30	7
TOC	mg/l	357	308
Conductivity	mhos	27600	32200
Sulfide	mg/l	0.6	106
Calcium	mg/l	5500	5500
Iron	mg/l	0.32	0.32
Lead	mg/l	1.0	1.0
TDS	mg/l	34590	34414
Silica	mg/l	15	15

- Step 2: Spike sample with approximately 710 mg of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and record pH.
- Step 3: Add appropriate chlorine dosage.
- Step 4: Collect incremental samples and analyze for sulfide content.

Results of the tests are presented in Table 23. The thirty minute reaction time was considered as the endpoint for scale up to full size. It is apparent that chlorine dosages greater than 1000 mg/l were excessive since the sulfide was oxidized to less than 10 mg/l in under five minutes. The low dosages of chlorine did not provide sufficient oxidation, so the range for large scale tests was established to be 400 mg/l - 1000 mg/l Cl_2 .

Aeration Tests

Preliminary tests for aeration involved two steps. In the first step, the rate of air addition was established. Tests were run at several air flow rates and the dissolved oxygen concentration was measured at different time intervals. The saturation oxygen level was measured to be 6 mg/l DO and it was reduced within one minute at an air flow rate of 0.023 l/sec (3 cfh). This flow rate was therefore used for further testing.

The aeration tests were then run in several types of containers. The most efficient transfer occurred in a cylinder with the longest contact time. However, to assure uniform comparisons, the full scale aeration tests would be run using the same apparatus as for chlorination.

Oxygenation Tests

Preliminary tests with pure oxygen were also performed at a gas flow rate of 3 cfh. The results of oxygenation were more effective than aeration, but not to a large degree. A comparison of the tests is shown in Table 24. However, it was determined that a full scale test of oxygenation was desirable.

UV Light Catalysis

It was hypothesized that radiation of the sample with UV light might provide a catalyst for the reaction to proceed at a higher rate. In order to test this theory, preliminary tests were performed using combined UV light with chlorination. The apparatus used is schematically illustrated in Figure 10. The UV light included a two bulb lamp which was placed 5cm (2 in.) from the surface of the wastewater. Two magnetic stirrers agitated the waste to allow exposure of a fresh thin liquid surface to the UV irradiation. The results are listed in Table 25 and selected comparisons of UV irradiated tests with non-irradiated tests are shown in Figure 11. It is apparent that additional UV light did not provide significant irradiation to allow extensive reaction rate increases. It is doubtful that in a full-scale operation, the resultant small benefits in rate increases determined that use of UV would not be cost-effective. Therefore, full-scale tests using UV light catalysis were eliminated.

TABLE 23. PRELIMINARY CHLORINATION TEST RESULTS.

Chlorine dosages mg/l	Sulfide residual, mg/l						
	222	443	665	886	1108	1330	1773
Contact time (minutes)							
0	107	100	107	115	107	107	107
1	---	---	25	---	4.3	<0.3	<0.3
2	---	40	---	25	---	---	---
4	---	36	21	---	3.1	---	---
5	---	---	---	21	---	---	---
7	62	---	---	---	---	---	---
10	---	34	18	14.5	---	---	---
15	53	---	---	---	0.9	---	---
20	---	31	15	---	---	---	---
30	41	21	12	4.6	0.3	---	---

TABLE 24. PRELIMINARY OXYGENATION AND AERATION TESTS.

Contact time (minutes)	Sulfide Residual, mg/l		
	Oxygenation	Aeration	Aeration
	1000 ml cylinder	1000 ml cylinder	beaker
0	107	107	107
5	94	107	102
10	90	103	99
15	---	103	94
20	85	---	---
25	---	100	91
30	78	---	---
35	---	95	85
40	75	---	---
45	---	87	65
50	72	---	---
55	---	79	47
60	67	---	---
65	---	67	25

TABLE 25. PRELIMINARY REACTIONS CATALYZED BY UV RADIATION.

Chlorine dose, mg/l	Sulfide residual, mg/l			
	222	443	665	886
Time (minutes)				
0	103	100	107	107
1	69	---	23	11
2	---	40	---	---
4	67	36	18	10
10	67	32	12	8
20	---	27	10	5
24	---	---	---	---
30	63	25	8	4

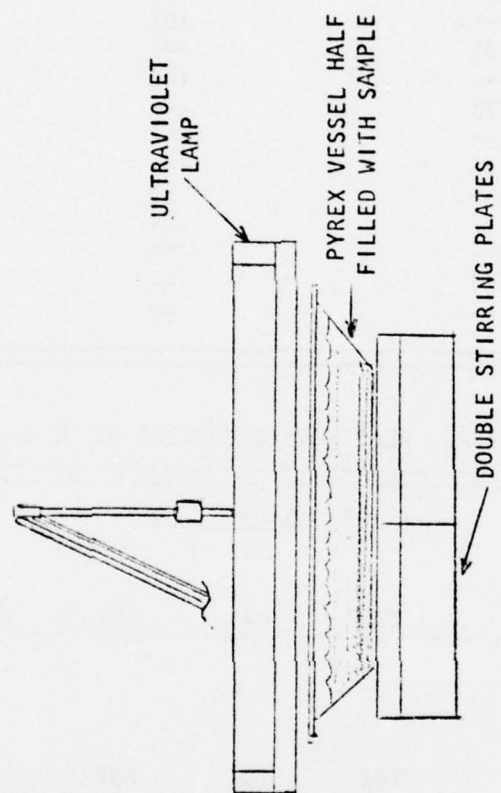


Figure 10. Schematic of UV irradiation device.

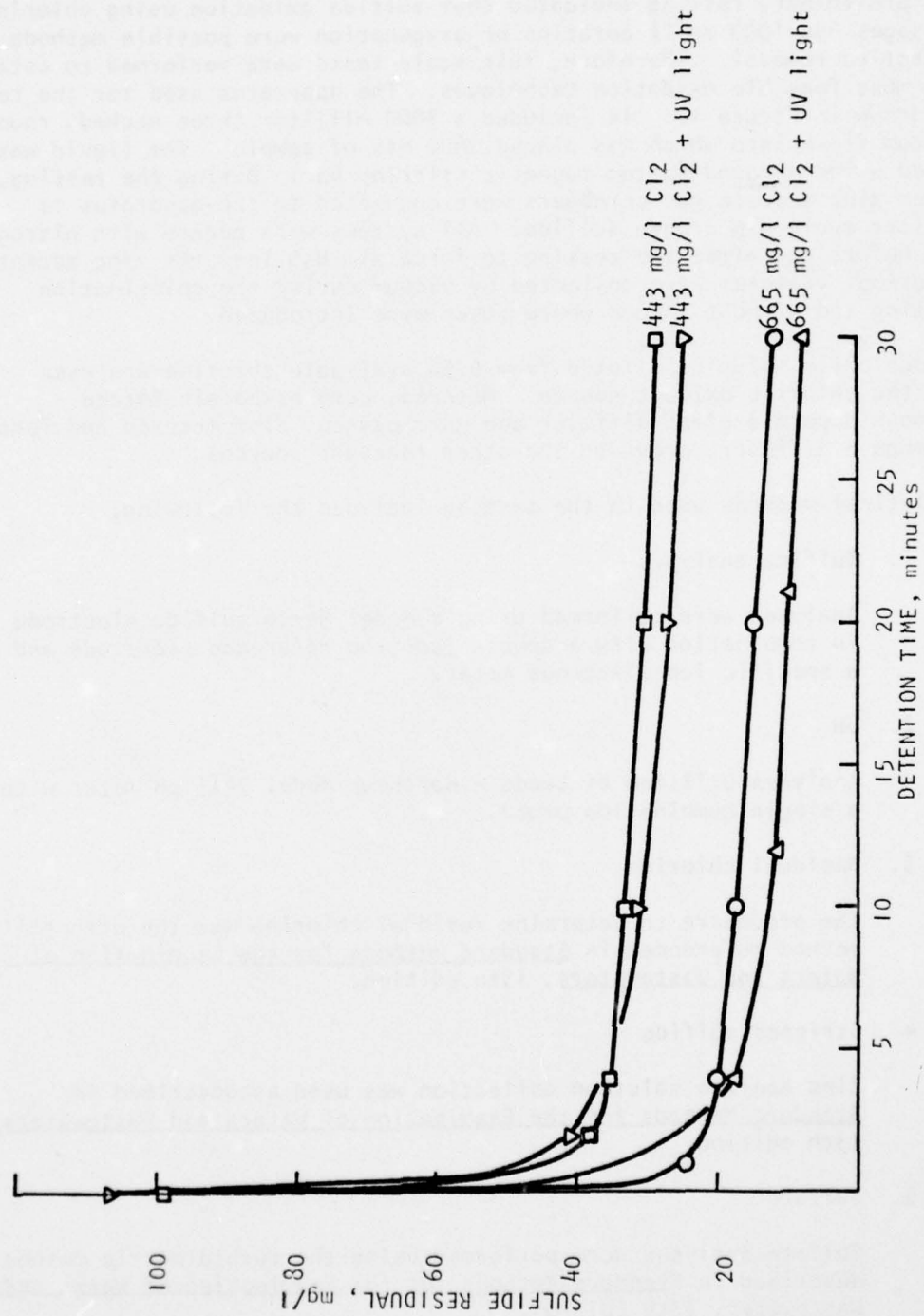


Figure 11. Selected comparisons between chlorination with and without UV light.

FULL SCALE RATE TESTS

General

The preliminary testing indicated that sulfide oxidation using chlorine, (dosages 400-1000 mg/l) aeration or oxygenation were possible methods for effective removal. Therefore, full scale tests were performed to establish the most feasible oxidation techniques. The apparatus used for the testing is drawn in Figure 12. It included a 3000 milliter three necked, round bottom flask into which was placed 2400 mls of sample. The liquid was mixed using a round bottom magnetic stirring bar. During the testing, three zinc acetate gas scrubbers were connected to the apparatus to collect evolved hydrogen sulfide. All systems were purged with nitrogen gas before and after the testing to force all H_2S into the zinc acetate solution. Samples were collected by vacuum during the chlorination testing and without vacuum where gases were introduced.

Hypochlorite solution diluted from 6.5% available chlorine was used for the chlorine oxidant source. Metered, compressed air forced through a porous glass diffuser and pure oxygen, also metered and forced through a diffuser, provided the other reactant sources.

Analytical methods used in the testing included the following:

1. Sulfide analysis

Analyses were performed using a Model 94-16 sulfide electrode in combination with a double junction reference electrode and a specific ion electrode meter.

2. pH

Analyses utilized at Leeds - Northrup Model 7415 pH meter with a single combination probe.

3. Residual chlorine

The procedure to determine residual chlorine was the orthotolidine method referenced in Standard Methods for the Examination of Waters and Wastewaters, 13th edition.

4. Stripped sulfide

Zinc acetate solution collection was used as described in Standard Methods for the Examination of Waters and Wastewaters, 13th edition.

5. Sulfate

Sulfate analyses were performed using the turbidimetric method described in Standard Methods for the Examination of Water and Wastewater, 13th Edition.

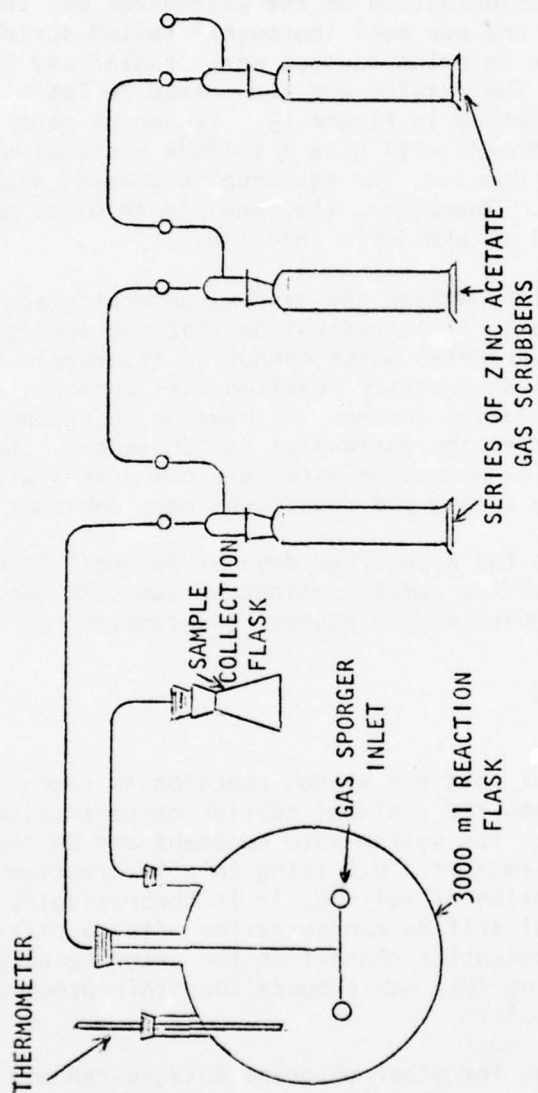


Figure 12. Schematic of reaction apparatus.

The main problem involved with the analyses was the difficulty in measuring small changes in sulfide concentration. The solution had a highly negative potential, so the expanded milli-volt scale could not be used. The solution also required two fold dilution to avoid formation of a heavy precipitate which coated the electrode and caused lower readings. Dilution eliminated this problem.

Chlorination Testing - Chlorination of the wastewater was the method which showed the most promise and was most thoroughly tested during the laboratory studies. Five different chlorine dosages were studied and the most feasible tests were replicated. The results are summarized in Table 26. The sulfide residuals are plotted in Figure 13. It can be seen that chlorine dosages greater than 600 mg/l will give a sulfide residual of less than 10 mg/l in 30 minutes. However, for scale-up to process size, a residual of 5 mg/l was desirable. Therefore, the required chlorine dosage was estimated to be 700 mg/l of available chlorine.

In order to more accurately define the system, general reaction rate constants were calculated. It is understood that the theoretical reaction is dependent upon many variables which cannot be accurately defined. However, it is possible to establish a system reaction rate constant given a specific wastewater system and chlorine dosage. It must be understood that the value defined is limited to the wastewater system tested. Changes in concentrations of chlorine demanding materials can drastically change the oxidant available in the system and reduce the rate constant.

The system rate constant for a chlorine dose of 700 mg/l is determined by a graph of inverse sulfide concentrations versus time shown in Figure 14. The slope of the line indicates the system rate constant as defined by the equation:

$$r = KC_S^2$$

Therefore, it is apparent that the system reaction is second order and the rate is dependent upon the residual sulfide concentrations at a specified chlorine dose. The system rate constant can be therefore calculated to be 0.004 l/mg-sec. Utilizing this information and knowledge of the initial concentration of sulfide, it is theoretically possible to calculate the residual sulfide concentration after a certain detention time. However, due to potential changes in the chlorine demand of other system constituents during full scale operation, this procedure will only yield an approximate result.

The system rate constants for other chlorine dosages can also be calculated using a graphical procedure. The results are listed below:

<u>Chlorine dose</u>	<u>Rate constant</u>
886 mg/l	0.591 l/mg-sec
753 mg/l	0.0126 l/mg-sec
700 mg/l	0.004 l/mg-sec

TABLE 26. FULL-SCALE SULFIDE REMOVAL TEST RESULTS - CHLORINATION.

Run No.	1		2		3	
Chlorine dosage	443 mg/l		665		665	
Time elapsed	Sulfide concentration	pH	Sulfide concentration	pH	Sulfide concentration	pH
0	106	11.2	106	11.2	112	11.2
0.5	46	---	25	---	23	---
1.0	40	11.0	18.4	10.9	22	10.95
1.5	38	---	17	---	21	---
2	36	---	15.6	---	20	---
3	35	10.9	14.3	10.9	19.5	10.95
4	34	---	14.3	---	19	---
6	33	10.9	14	10.9	18	10.9
8	32	---	13.2	---	16.4	---
10	32	10.9	12.6	10.8	15.4	10.9
15	30	---	9.2	---	11.4	---
20	30	10.9	8.0	10.8	9.8	10.95
25	29	---	7.2	---	8.5	---
30	28	---	6.8	---	7.8	---
40	27	10.8	6.8	10.8	7.5	10.8
50	26	---	6.6	---	7.2	---
60	25	---	6.4	10.75	6.9	10.75
Stripped S =	0.076		0.8		0.09	

TABLE 26 (continued).

Run No.	4		5		6		7	
Chlorine dosage	700		700		753		836	
Time elapsed	Sulfide concentration	pH	Sulfide concentration	pH	Sulfide concentration	pH	Sulfide concentration	pH
0	106	11.2	106	11.2	112	11.2	106	11.2
0.5	15.4	---	16.6	---	14.4	---	11.6	---
1.0	12.9	11.05	13.4	11.05	11.0	11.05	1.3	10.9
1.5	12.4	---	12.8	---	10.6	---	1.1	---
2	11.9	---	12.4	---	10.3	---	0.8	---
3	11.4	11.05	11.9	11.0	9.4	11.05	0.6	10.9
4	10.6	---	11.4	---	8.5	---	<0.6	10.9
6	9.8	11.0	11.0	10.95	7.3	11.00	<0.6	---
8	9.0	---	10.6	---	6.0	---	<0.6	---
10	8.5	10.95	9.8	10.95	5.0	10.95	<0.6	---
15	6.8	---	8.1	---	3.6	---	<0.6	---
20	6.0	10.85	6.8	10.9	2.7	10.9	<0.6	---
25	5.4	---	5.4	---	2.3	---	<0.6	---
30	5.0	10.85	5.0	---	2.0	10.85	<0.6	---
40	4.2	10.8	4.2	10.85	1.8	10.8	<0.6	---
45	3.9	---	---	---	---	---	<0.6	---
50	3.6	---	3.6	---	1.5	---	<0.6	---
60	3.2	10.8	3.4	10.8	1.2	10.8	<0.6	10.8
Stripped S =	0.69		0.85		0.09		0.06	



Figure 13. Full-scale chlorination tests for sulfide removal.

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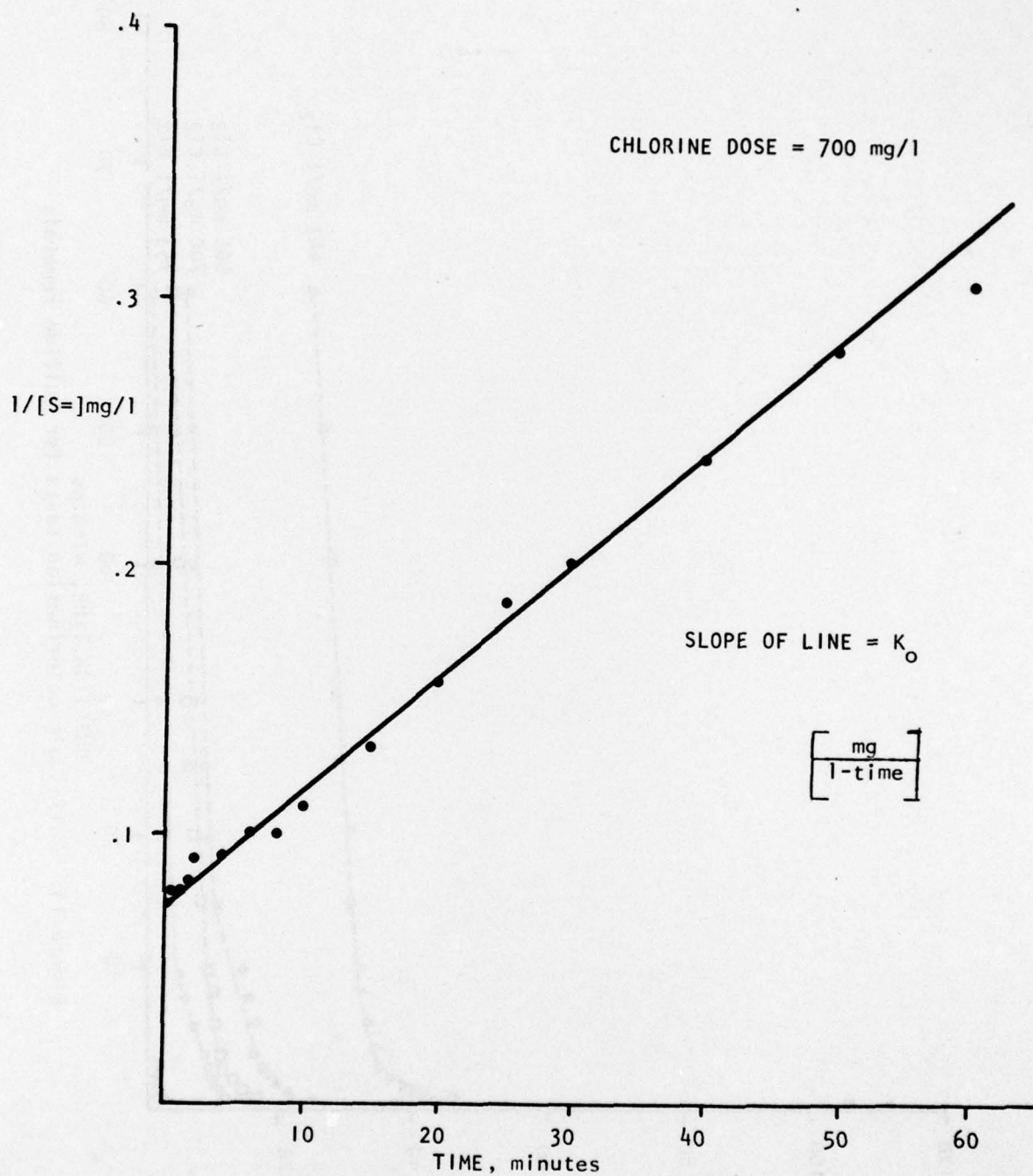


Figure 14. Rate constant graphical determination.

665 mg/l
443 mg/l

0.00211 l/mg-sec
0.000243 l/mg-sec

The change in system rate constant with chlorine dose can be possibly explained by considering that other chlorine demanding substances are present in the wastewater which remove the available oxidant prior to the sulfide/chlorine reaction. Therefore, the needed excess of chlorine is not as available to the sulfide complex. However, all results indicate that the system oxidation reaction is second order in each case.

Oxidation with Air and Oxygen - Oxidation of the wastewater with air or pure oxygen was considered a potential approach to oxidation of the sulfide without expensive chemical addition. The preliminary tests indicated that an air injection rate of 0.023 l/sec (3cfh) was sufficient to saturate the wastewater quickly and this flow rate was used in all testing. The results of the tests are included in Table 27. The variation in sulfide residual versus time is plotted in Figure 15. It can be seen that these systems are more complex than chlorination. The results did not allow the sulfide concentration to be reduced below 10 mg/l even after a sixty minute reaction time. Therefore, neither aeration nor oxygenation were desirable for use in oxidizing the NG-1 waste stream, and further analyses were not undertaken.

ECONOMIC ANALYSES OF SULFIDE REMOVAL METHODS

General

Laboratory tests indicated that sulfide oxidation to allow residual concentrations of 10 mg/l could be accomplished using chlorination only. However, there are several alternative methods to use in accomplishing chlorine addition including direct injection into a previously used process tank or a new tank, dry chlorine use or liquid chlorine addition, etc. The costs for feasible alternatives were calculated and are presented in this section. In addition, the feasibility of dilution to reduce sulfide concentrations to below 10 mg/l was determined. All results are presented in the following paragraphs.

Alternatives Considered

There were four alternatives considered in developing the most economical method of chlorine injection. The desirable dosage of 700 mg/l available chlorine was maintained for all systems and a maximum NG-1 system flow rate of 47,100 gpd was utilized: The alternatives considered are as follows:

1. Sodium hypochlorite (liquid) addition to new tank.
2. Calcium hypochlorite (solid) addition to new tank.
3. Sodium hypochlorite (liquid) addition to process tank.
4. Calcium hypochlorite (solid) addition to process tank.

In addition, the required volume of waste stream to provide dilution of the sulfide to acceptable limits was considered.

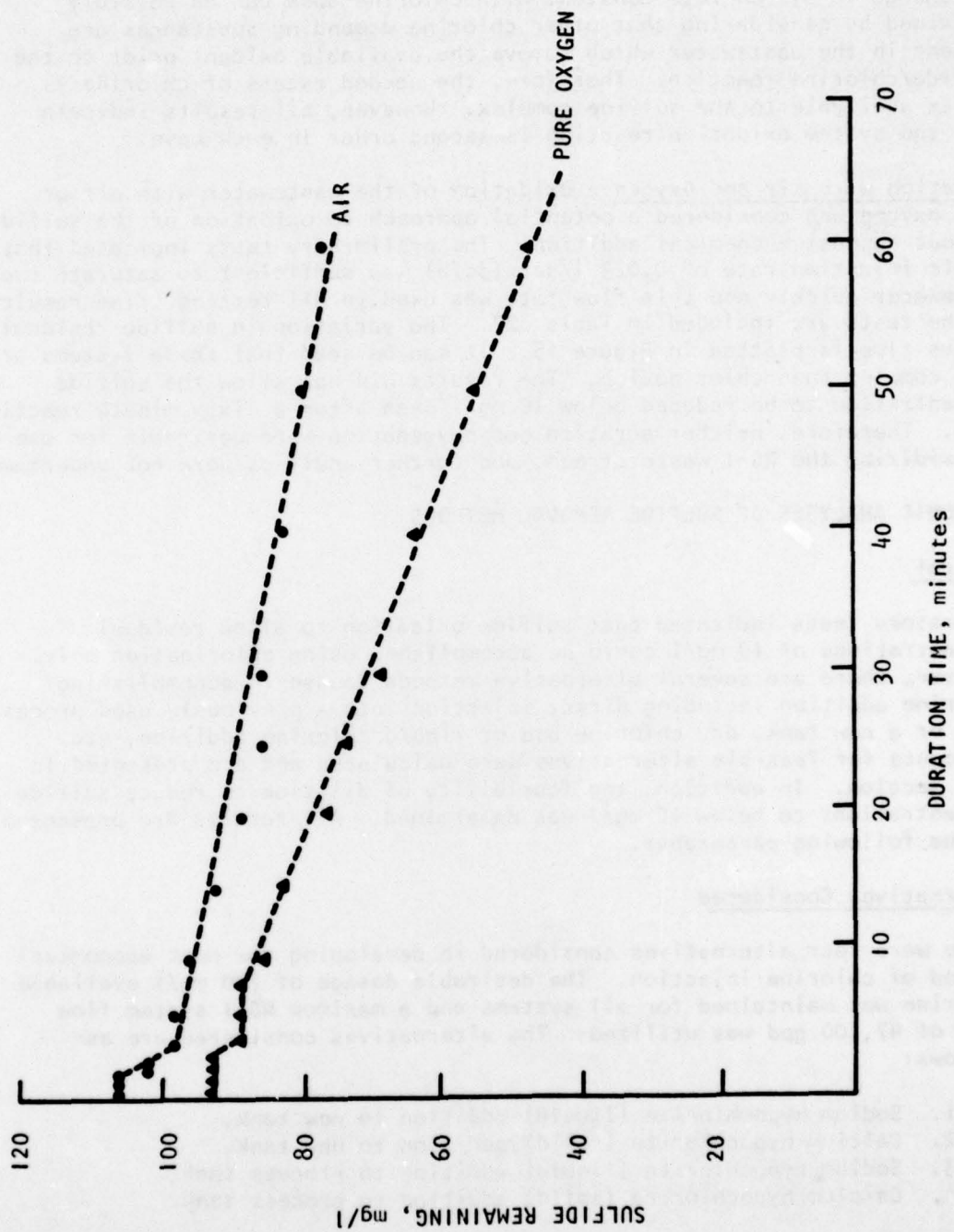


Figure 15. Sulfide oxidation with air and oxygen.

Technical Feasibility

Use of sodium hypochlorite and calcium hypochlorite as oxidant sources were investigated with respect to their overall technical feasibility in this application. Sodium hypochlorite was found to have several significant advantages including lower cost and the ability to be fed directly into the chlorination tank without dilution. However, the material is available only in a liquid form which is somewhat unstable. A maximum holding time of thirty days was recommended by the manufacturer, therefore, relatively frequent deliveries would be required. Also, if the chemical would not be readily available from the manufacturer, an immediate shortage could occur.

Therefore, the use of solid calcium hypochlorite was considered. This material is more costly but it could be mixed in various size batches for field use. However, when preliminary investigations of system design were begun, severe materials handling problems were established. This problem was most apparent when the use of a bin feeder was investigated. The manufacturer emphatically stated that their equipment (and similar equipment) could not be used in this application. This factor, along with a significant higher chemical costs, indicated that further consideration for use of calcium hypochlorite was not technically or economically feasible.

Process Equipment for Sodium Hypochlorite Addition

Various types of equipment are needed to provide controlled addition of sodium hypochlorite. The first requirement is a specially chosen tank to contain the 15% solution at the application site. Since large quantities of solution are needed, the most economical shipping size is in tank cars with volumes of 17-19 m³ (4500-5000 gals.). These must be unloaded and the volume stored on site. Therefore, a 22.7 m³ (6000 gal.) covered storage tank is needed. This size will allow a safety factor of approximately 3.8 m³ (1000 gallons) or 5.5 additional days of use between fills.

Since large volumes of chemicals are needed and since it is anticipated that the wastewater stream could vary significantly in volume, a feedback flow control system has been proposed. This system would include flow measurement by a parshall flume and then transferral of the signal through a controller to a metered chemical feed pump. The pump, feeding from the storage tank, would therefore, add the specified volume of chlorine to the system. In general the material would be placed in the line or added with a simple diffuser in the tank.

Cost Estimates

Cost estimates have been established for sodium hypochlorite addition directly into the proposed clarifier or separately into a 7.5 m³ (2000 gal.) reaction tank. Care must be taken to insure that the construction of the large clarifier is suitable to handle chlorine concentrations of 706 mg/l,

however, this is not an extremely severe application.

The estimated capital costs are listed below:

<u>System</u>	<u>Component</u>	<u>Cost, \$</u>
Pumping system	Pump	\$1,110
	Stroke control	900
Piping (50 ft of PVC)		250
Control system	Flume	1,100
	Transmitter	800
	Ratio unit	700
Storage	Tank	2,690
	Accessories	550
Control panel (wiring)		1,000
Reaction tank	Tank	1,425
	Accessories	550

It is assumed that installation costs will be approximately 30 percent of the total capital expenditure. Therefore, the capital costs for the two alternatives are summarized in Table 28.

Operating costs are almost entirely chemical costs to provide for the extremely high chlorine doses needed. Calculations indicate that an average sodium hypochlorite dose is 700 l/day (185 gal./day). Therefore, annual chemical costs are approximately \$29,710 with additional equipment operation and maintenance costs of \$1,360/year for alternative one and \$1,650/year for alternative two. Total operating costs are estimated to be \$31,070/year for alternatives 1 and \$31,360/year for alternative 2.

Use of Dilution for Sulfide Removal

Since chemical costs for effective oxidation of chlorine are very high, it is desirable to possibly reduce concentrations of sulfide by dilution of the stream. The maximum concentration of sulfide allowable in biological influent is 10-25 mg/l depending upon the individual system tolerances and discharge limitations. If it is assumed that a 10 mg/l sulfide concentration is required, then the volume of dilution water needed is calculated using the following formula:

$$V = \frac{4.239 \times 10^6}{10-y}$$

V = gallons of dilution water

y = sulfide concentration in
dilution water (mg/l)

gallons $\times 3.78 \times 10^{-3} = m^3$

TABLE 27. FULL-SCALE AERATION AND OXYGENATION TESTS.

Run No.:	1	2	3
Time elapsed	Air oxidation	Air oxidation	Oxygen oxidation
0	106	106	106
0.5	106	106	92
1.0	106	106	92
1.5	106	106	92
2.0	102	106	92
3.0	102	106	92
4.0	98	106	88
6.0	98	106	88
10.0	98	106	85
15.0	96	106	82
20.0	92	106	76
25.0	88	106	73
30.0	85	83	68
40.0	85	---	63
50.0	82	---	54
60.0	77	---	46

TABLE 28. ALTERNATIVE COSTS FOR CHLORINATION.

Alternative number	System	Cost, \$			
		Capital cost	Inst. cost	Contingency 15%	Total
1	Sodium hypochlorite addition/existing clarifier	\$ 9,100	\$2,750	\$1,780	\$13,630
2	Sodium hypochlorite addition/new reaction tank	11,075	3,325	2,160	16,650

Therefore, the minimum volume of dilution water is 1604 m^3 (423,900 gallons) if no residual sulfide is present in the dilution stream.

RECOMMENDED METHOD FOR SULFIDE REMOVAL

If possible, the most cost effective method for sulfide removal is dilution. The diluting influent stream must have a sulfide residual of less than 10 mg/l and the volume required will vary from 1604 – $16,040 \text{ m}^3$ (423,900 – 4,239,000 gallons). Bleed in of the NG-1 stream, over twenty-four hours would be the most feasible approach.

If dilution water is not available in sufficient quantities, it is recommended that 15% sodium hypochlorite solution be added to the wastewater in a separate 7.5 m^3 (2000 gal.) reaction tank. This system will allow a full one hour reaction time, (based on a maximum system flow rate of $178 \text{ m}^3/\text{day}$ (47100 gal. per day)). Although this approach is more costly than adding the solution directly to the proposed clarifier, it provides a safer system with respect to potential corrosion problems in the larger clarifier. It will also allow more system control. The approximate capital costs are \$16,560 with associated operating costs of \$31,360 annually.

SECTION VIII

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